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Water chemistry of Afra and Burbeita hot springs and its impact soil irrigated its water

By
Mohammad Ibrahim Mohammad Amiriyyin

Supervisor
Prof. Dr. Anwar Jiries

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Dedication

To My Family

Father , Mother,

Brothers , Sister

Mohammad Ibrahim Amiriyyin

Acknowledgment

First praise to Allah who helped me to complete this thesis.

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I would like also to thank Jordan Abyad Fertilizers and Chemical Company for their help and cooperation in analyzing the samples and in particular the chemist Mr. Mohammad Sahel Al-Bderat who helped me in the analysis .

Mohammad Ibrahim Amiriyyin

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List of Symbols and Abbreviations

AgCl : Silver chloride
$AgNO_3$: Silver Nitrate
$BaSO_4$: Barium sulphate
BR : Burbeita spring
Ca^{+2} : Calcium ion
$CaCO_3$: Calcium carbonate
Cl^- : Chloride ion
Co : Cobalt metal
CO_2 : Carbon dioxide
Cr : Chromium metal
Cu : Copper metal
EC : Electrical Conductivity
EDTA : Ethylene Diamine Tetra acetic acid
Fe : Iron metal
FSAA : Fast Sequential Atomic absorption
HM : Heavy metal
HCl: hydrochloric acid
HCO_3^- : Bicarbonate ion
HNO_3 : Nitric acid
IB : Ion balance
JISM : Jordan institution for standards and metrology
K^+ : Potassium ion
Max : maximum
meq : milli equivalent
Mg^{+2}: Magnesium ion
Min : Minimum
MPCL: Maximum permissible concentration level
Na^+: Sodium ion
Ni : Nickel metal
NO_3^-: Nitrate ion
Pb : Lead metal
pH: potential of hydrogen
ppb: part per billion
ppm : part per million
PVC: poly(vinyl chloride)
SO_4^{-2}: Sulphate ion
Sp : Afra spring
STD : Standard Deviation
TDS : Total Dissolved Solid
TH : Total hardness
USDA : United state department of agriculture
WHO : World health organization
Zn : Zinc

Abstract

Water chemistry of Afra and Burbeita hot springs and its impact soil irrigated its water.

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Evaluation of water quality of Afra and Burbeita Hot springs and evaluation the quality of soil irrigated with their Hot springs was done. Sampling was done for two seasons one at the end of the winter season 2011 and one at the end of the summer season 2012.

The evaluation was in terms of its inorganic constituents including major ionic composition (HCO_3^-, Cl^-, NO_3^-, SO_4^{-2}, Ca^{+2}, Mg^{+2}, Na^+ and K^+) in water and six heavy metals (Co, Zn , Cr ,Cu , Fe , Ni) in both water and soil irrigated with these springs.

The results showed that the temperature and salinity of both sites were constant with time indicating that the rainy season do not play an important role in the water temperature and salinity and the water type of both sites can be considered as calcium magnesium type with prevailing sulfate and chloride.

The outlet at Afra site showed a significant increase in Ca concentrations at the end of summer season which can be due to evaporation of the thermal water during hot and dry summer conditions increased with the high temperature of the thermal water.

The quality of springs at both sites (Afra and Burbeita) was evaluated for irrigational purposes. The results showed that both were of medium electrical conductivity and low sodium hazard indicating that the water can be used for irrigational purposes without risk.

Regarding heavy metals (HM), the abundance of Heavy metals at both sites was showed similar and they were in descending order Fe> Co > Ni>Cu >Zn while Cr was not detected in any sample, the highest metal was iron which is due to the litho- logy of the aquifer. The (HM) concentrations were very low which was attributed to neutral pH of the water enhancing its precipitation from the liquid phase to the solid phase which was marked by the inverse relationship between heavy metals concentration in soil with water as some heavy metals found below detection limit in the aqueous phase. The highest heavy metals concentration in the soil indicating its precipitation to the soil surface.

الملخص

تقييم نوعية المياه من ينابيع عفرا وبربيطة ونوعية التربة المروية بمياه هذه الينابيع

محمد إبراهيم العميريين

جامعة مؤتة، 2012

في هذه الدراسة تم تقييم نوعية المياه من ينابيع عفرا وبربيطة الواقعة في محافظة الطفيلة جنوبي الأردن وتقييم نوعية التربة المروية بمياه هذه الينابيع، تم اخذ العينات خلال موسمي الصيف والشتاء في سنة 2012.

كان تقييم نوعية المياه من حيث مكوناته الغير عضوية مثل الايونات الموجبة (الكالسيوم والصوديوم والمغنيسيوم والبوتاسيوم، والايونات السالبة مثل (الكبريتات، النترات، الكلوريد، الكربونات) وبعض العناصر الثقيلة وهي (الحديد، النيكل، الكوبالت، الكروم، الخارصين، النحاس) في كل من المياه والتربة المروية بمياه هذه الينابيع.

أظهرت النتائج أن درجة الحرارة والملوحة في كلا الموقعين هي ثابتة بمرور الوقت وهذا يشير إلى أن الموسم المطري ليس له أي تأثير كبير على درجة الحرارة أو الملوحة، ويمكن اعتبار أن نوعية المياه في كلا الموقعين هي غنية بالكالسيوم والمغنيسيوم مع الكبريتات والكلوريد كعناصر سائدة.

كما تشير النتائج إلى أن المياه الممتزجة من جميع الينابيع مع بعضها في موقع عفرا تحتوي على تركيز عالي من الكالسيوم في نهاية فصل الصيف وهذا مرده إلى ارتفاع درجة حرارة المياه في فصل الصيف.

أما بالنسبة إلى النشاط الزراعي فليس له أي تأثير على نوعية المياه الجوفية بموقعي عفرا وبربيطة نضرا إلى موقعهما خارج منطقة تغذية هذه الينابيع. أما بالنسبة لنوعية المياه في كلا الموقعين المستخدمة في ري المحاصيل الزراعية في منطقتي الدراسة حيث أظهرت النتائج أنها ذات ملوحة متوسطة وتصلح لري اغلب المحاصيل الزراعية كما أن نسبة الصوديوم المتبادلة فيها منخفضة.

كما بينت الدراسة بان تراكيز العناصر الثقيلة في المياه والتربة في كلا الموقعين كانت منخفضة بسبب الحموضة المعتدلة للمياه التي تساعد في ترسيب هذه العناصر ،كما أن هناك علاقة عكسية مابين تراكيز العناصر في المياه مع التربة،حيث كان تركيزها بشكل تنازلي كما يلي Fe> Co > Ni>Cu >Zn>Cr .

أظهرت النتائج أيضا أن تركيز الحديد في المياه في كلا الموقعين مرتفع وذلك بسبب نوعية الصخور الحاملة لهذه المياه .

Chapter One
Introduction

Water is an essential requirement of human and industrial developments and it is the most delicate part of the environment [Das and Acharya 2003]. "Water quality deals with the physical, chemical and biological characteristics in relation to all other hydrological properties" [Atulegwu and Njoku 2004].

Jordan can be described as one of the most water-scarce countries, due to a semiarid climate and a population that is increasing at about 3.5% annually. Agricultural activities in Jordan consume more than 65% of its available water resources including treated wastewater and fresh groundwater including thermal springs as well as surface water.

A spring is described as a concentrated discharge of groundwater that appears at the surface as a current of flowing water (Todd, 1980). Springs that discharge water with a temperature above that of the normal local groundwater are called thermal springs (Todd, 1980). Thermal springs are natural geological phenomena that occur on all continents, in Jordan there are more than ten thermal spring distributed mainly along the eastern flank of the Jordan valley (Figure 1). A number of hot springs in Jordan have been developed for recreational and tourism purposes such as Main thermal springs and to lower extend Afra and Burbeita thermal springs as hot or warm water can hold more dissolved solids, warm and especially hot springs also often have a very high mineral content, containing everything from simple calcium to lithium, and even radium. Because of both the folklore and the claimed medical value some of these springs, they are often popular tourist destinations, and locations for rehabilitation clinics for those with disabilities.

There is no definite definition for thermal springs but the most convenient definitions are :

1. A type of thermal spring in which hot water is brought to the surface. The water temperature of a hot spring is usually 6.5 °C or more above mean air temperature . by this definition " thermal spring " is not equivalent with the term " hot spring " (Leet 1982).
2. A spring whose hot water is brought to the surface. The water temperature of the spring is usually 8.3 °C (15 °F) or more above the mean air temperature (Nalms 2007)

An important feature of present geothermal activity in Jordan is that it is expressed entirely in the form of thermal springs and most of them are located along a distance of about 200 km on the eastern side of the Rift, extending from Yarmouk River in the north to Tafila in the south with temperatures ranging from 30 to 63^{o}C along the Jordan rift valley where it was assumed that the water is heated through the hot igneous rocks beneath these springs but recently Swarieh 2008 reported that the heat source of the

thermal water in the lower aquifer is a result of the deep circulation of water within the Paleozoic sandstones receiving heat from a normal to slightly elevated geothermal gradient.

The physical and chemical parameters of groundwater play a significant role in classifying and assessing water quality. The hydro chemical study reveals quality of water that is suitable for irrigation, agriculture, drinking and industrial purposes

The water chemistry of thermal springs is a combination of many factors through the hydrological water cycle of the water. These factors are the chemical composition of airborne particles in the atmosphere that influence the meteoric water composition, rock composition where water is stored and flows through.

Therefore, the chemistry of spring waters reflects the interaction of groundwater with the aquifer host rock as well as any chemical constituents that may be introduced from surface sources. Spring water chemistry is not intrinsically different from groundwater chemistry and the same principles apply. Aqueous chemistry in general and spring water chemistry in particular, can be approached from two points of view. One can begin with the minerals that make up the host rock and their thermodynamic properties and calculate mineral solubility and interactions. From this, in principle, the water chemistry can be predicted. The common cations in spring waters are Ca^{2+}, Mg^{2+}, Na^{+}, and K^{+}; while the most common anions are HCO_3^{-}, SO_4^{2-}, NO_3^{-} and Cl^{-}. The dominant chemistry usually depends on the host rock of the aquifer from which the spring emerges.

1.1.Heavy metal in aquatic environment

The solubility of many minerals increase with increasing temperatures which makes thermal water able to dissolve minerals over time. Therefore, elevated level of metal and metalloids are often associated with hot springs (Stauffer et al. 1980).

The term "heavy metals" refer to any metallic element that has a relatively high density and applies to the group of metal and metalloids with atomic density greater than 4g/cm^3. Heavy metals are well known to be toxic to most organisms when present in high concentration in the environment (Batayneh, 2010) .

Heavy metals become toxic when they are not metabolized by the body and accumulate in the soft tissues. They may enter the human body through food , water , air, or absorption through the skin when they come in contact with humans in agriculture and in manufacturing , pharmaceutical , industrial , or residential settings(http://www.lef.org).

1.2.Study Area

location

The study area, Afra and Burbeita geothermal area, is located about 200 kilometers south of Amman city, in south Jordan, on the western limb of Sharah Mountain (Figure 1) . This geothermal system consists of two springs with discharging temperatures between 45 to 48 ^{o}C . The thermal water of these springs is presently flows through open channels to pools, where it used for swimming and as a treatment for skin diseases.

Tafila province is characterized by a large number of springs which was reported to be around 360 springs discharging along the western part of the province. The investigated springs, Afra and Burbeita originated from the lower cretaceous sandstone underlying the gravel (Harahsheh .S, 2002).

The thermal water of Afra flows from more than 15 springs along the course of wadi Afra which is located in northern Tafila city and extends between longitudes (35 ′38) , and latitudes (30 ′52) and (31 ′00) (Ministry of Tourism, 1997).

The average flow rate is around 500 liter per second, there are six small sized pools and large squares allow people to setup camps, including indoor pools especially for women in addition to a room for steaming purposes in addition to a pool with a moderate temperature spring originated from a different aquifer.

Burbeita springs are located 3km north of Afra springs and it consists of two springs of different temperatures. One of them discharge warm water filling one of the pools, and the other spring is a normal temperature and it is used for drinking purposes.

The water of Afra can be used to cure some diseases such as arthritis, chronic arthritis, peripheral circulation troubles, muscular contractions, and muscle cramp, regulation of gland secretions, gynecological diseases, infertility problems, nervous restorations and rheumatism . the ministry of tourism has developed the site in 1997, 2002, 2004 and 2007. the number of visitors to the Afra site in 2012 reached to 26,161. (Ministry of tourism).

Burbeita and Afra sites are very close to each other with similar topography and rock types such as granite rocks being the major component in this region (Saqan et al , 2000)

Climate:

the investigated area has a Mediterranean climatic conditions characterized by hot and dry in summer and cool ,rainy winters. the Mean minimum and maximum temperature in the study area are -4^{o}C in January, especially in the night, and 38.5^{o}C in August .Rainfall occurs only in the winter season , which is extended from November to April , The average precipitations is around 250mm, Snowfall occurs occasionally, mainly in the highlands, during the period between January and March. the mean

number of days with snow is around seven days per year and the maximum recorded annual snowfall is 50 cm to 75cm. the prevailing wind direction is from westerly to northwesterly (Al-Rawajfeh and Al-Shamaileh ,2006).

Agriculture

The effluent water produced from Afra and Burbeita is used for agricultural activities.

In Afra, the water is used to irrigate fields planted mainly with vegetables such as tomato, cucumber and beans. The planted area using this source of water is located downstream at the Jordan valley.

In Burbeita, the agricultural activities are located up stream at site of the spring. the water is used to irrigate trees such as olive, guava, citrus and others.

1.3.Objectives

The main objectives of this study is to evaluate the chemical and physical parameters of Afra and Burbeita thermal water, in terms of its major ionic chemistry and its heavy metals concentrations, as well as to find the impact of using the water from these spring, on the heavy metals contents of soil irrigated with this water.

To achieve the objectives of the study, the following questions should be answered :

1. Are there heavy metals in Afra and Burbeita springs? If so - in what concentrations?
2. How are they distributed with respect to water and sediment phases?
3. In what relative proportions are they present within each phase?
4. How do chemical parameters and concentrations of heavy metals change between the field trips?
5. Is the thermal water is suitable for irrigation purposes.
6. Is there any impact of using Afra and Burbeita thermal water on soil irrigated with these types of water?

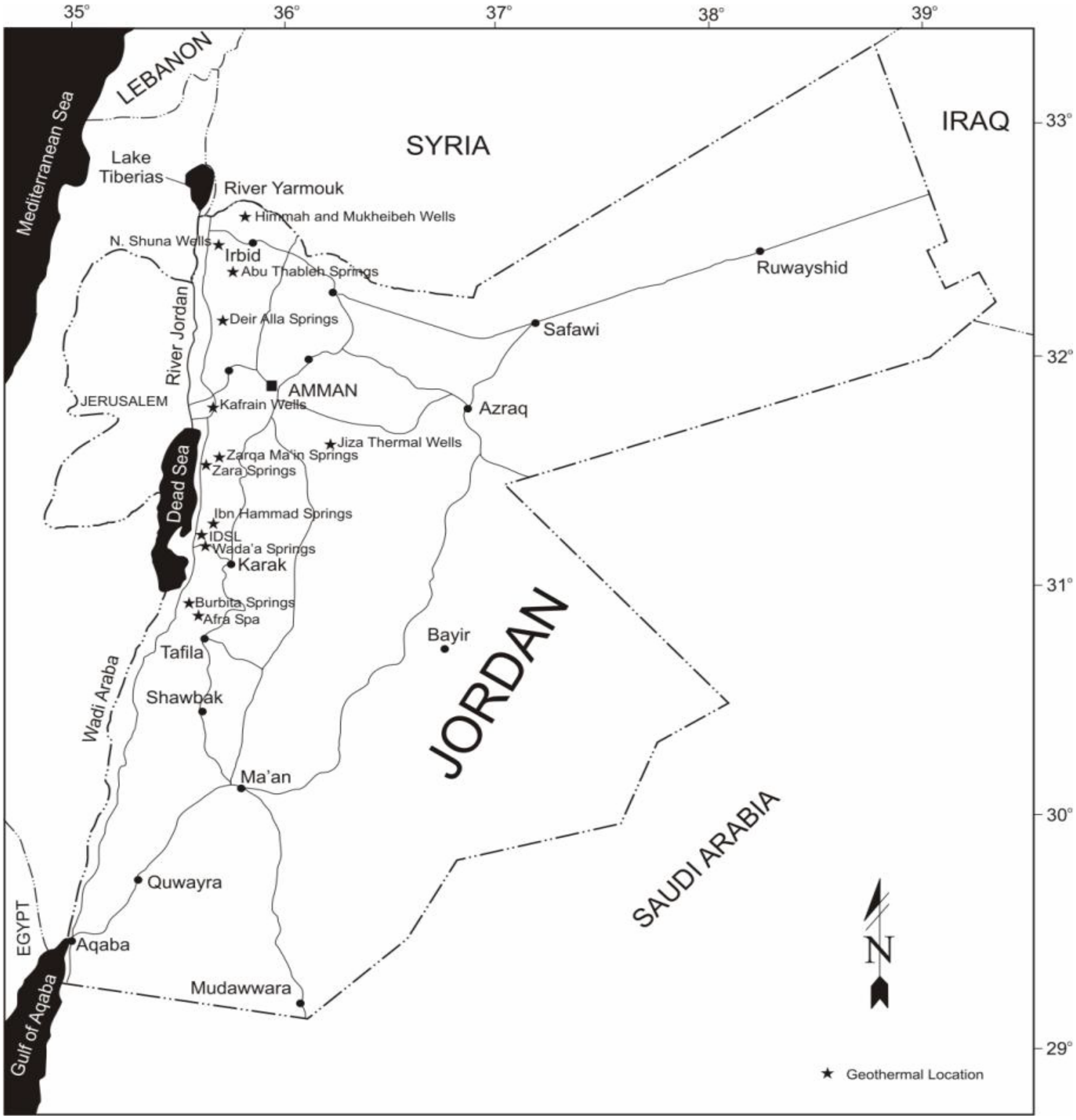


Figure 1
Jordan and geothermal resource locations including investigation area (After Sawarieh 2008) .



Figure2
Afra map

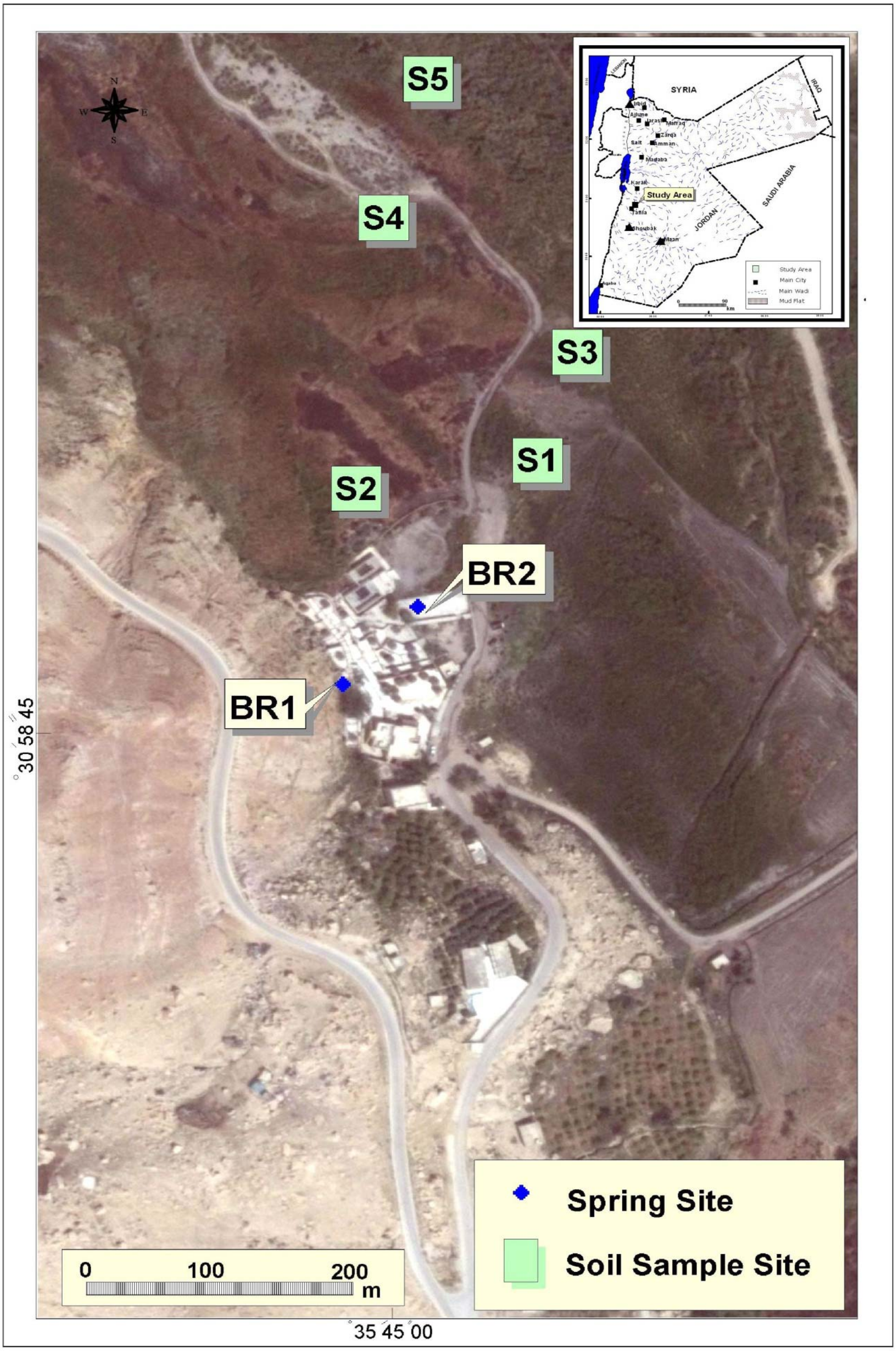


Figure 3
Burbeita map.

Chapter Two
Literature Review

Many studies had been conducted to investigate the water chemistry of hot springs . In general, the chemical composition of springs and ground water are often a good indicator for understanding the subsurface environments.

Salameh and Rimawi ,(1988) found that the elevated temperature of the water in the reservoir (73–82°C) is attributed to the presence of a heat-storing layer topping the aquifer.

Saline versus fresh water contribution to the thermal water of the northern Jordan rift valley, was investigated by Arad and Bein 2007 where they found that the temperature and salinity differences between thermal waters at equal depths on both sides of Lake Tiberias, reveals that the hotter eastern system consists of heated fresh groundwater, whereas the western system consists of heated saline groundwater.

Hot water is able to dissolve minerals over time, so that elevated level of metal and metalloids are often associated with hot springs (Iris Koch et al 1999).Water from hot springs in Yellowstone national park was investigation by Stauffer et al (1980), they showed that the concentration of some heavy metals such as arsenic (As) reached a concentrations of 1.6ppm (Stauffer et al , 1980).

The hot spring water of la selva geothermal system at Giron.a,North east Spain was investigated by Navaro et al. 2011 where they found high concentrations of (Cl , F , Ca ,Na ,K ,Li ,Si ,As , Ba ,Rb,) , whereas cold water show low salinity and high concentration of nitrate (NO_3^-).

The chemistry of hot springs along the Eastern Lau spreading center at west of the Tonga were studied by Mottle et al 2010 ,the result showed an increase in the concentration of soluble elements such as K , Rb , Cs , B due to the thermal effect of the water.

The major dissolved component (in ppm) of Bandaiko hot spring , Gunma, Japan water was investigated by Kikawada and Kawai, (2004) where they found that some heavy metal such as arsenic concentration increased drastically in mid 1980s , until reached in late 1990s about 10 mg /L in 2002 .(Y. Kikawada, S. Kawai, T. Oi , 2004).

Hot springs of Rhodesia: Their noble gases, isotopic and chemical composition were studied by Mazor and Verhagen (1976) They concluded that the chemical composition of the waters clearly reflects their origin from two groups of rocks - one from Karroo sediments and one from crystalline rock (Mazor et al,1976) .

The concentration of (Zn) in hot spring Champagne pool in New Zealand reached 50 ppm (Weissberg , 1975).

Basahy (1994) investigated the water chemistry of two natural hot spring in the Gizan area (Ain Al –Harra T= 50 ^{o}C) ,(Ain Al- Khoba T = 57^{o}C) in Saudi Arabia. He found that the elements Iron , manganese , zinc , were present in low quantity which was attributed to its low concentration in the host aquifer .

The six hot springs from Vinadio and the springs from Valdieri (Piemonte, Italy) have similar emergence temperatures (50^{o}C), similar deep temperatures (115 ^{o}C) and their chloride content varies from 0.9 to 30 mmol/kg, Major elements and some trace elements concentrations(Ba , Rb , Cs, Li, Mn) correlate closely with Na concentrations (Michared et al, 1989).

Obuki Tamagawa hot spring , Japan showed a very high sulfate concentrations where it ranged from 810 to 3000 mg/L over 30 years, and sulfate concentration increased steadily from 1972 to its maximum concentration in 1978, and then decreased steadily from 1978 to its minimum concentration in 1991, and the chloride ion concentration ranged (from 2310 to 3380 mg/L), and also reached a maximum in 1978; and then decreased to a minimum in 1991 (Yoshiike, 2003).

The Hammat Gader (El-Hamma) springs of occupied Palestine constitute a rift valley hot-spring system. The five springs which belong to this complex are distinguished by temperatures of 25, 28, 36, 42 and 50°C and salinities of between 700 and 1400 mg/l. With one exception, the salinity of the spring waters increases with temperature (Avraham et al ,1979).

A study done by (El-Zain et al 2002) to investigate the quality of hot springs water in parts of Jebel Mara Area mountain, Sudan, reveals that most waters taken from hot springs has high values of Hydrogen ion concentration (pH), electrical conductivity (E.C), high concentrations of total hardness (T.H), total dissolved solids (T.D.S) , bicarbonates (HCO_3), sodium (Na) and Magnesium (Mg). High pH, T.D.S, T.H, Na and HCO_3 are mainly due to dissolution of these ions from rock bearing minerals of the study area. Normal values of trace elements like Iron (Fe), Copper (Cu), , and Zinc (Zn) whereas, high concentrations of Manganese (Mn) (above the recommended values given by W.H.O., 1984), They classified hot springs waters as Calcium - Magnesium- Sodium Bicarbonate type Using U.S.D.A.(1954) classification, water has been classified as C2 S1that mean medium conductivity-salinity and low sodium content (http://www. Engineering civil.com).

Thermal springs associated with normal faults in Utah have been analyzed for major cations and anions, and oxygen and hydrogen isotopes. Springs with measured temperatures averaging greater than 40°C, are characterized by Na^+, K^+ and SO_4^{2-} ,Cl^- rich waters with total dissolved solids of 103 to 104 mg/l. Lower temperature springs, averaging less than

40°C, are more enriched in Ca^{+2} Mg^{+2} relative to Na^{+} K^{+}. Chemical variations monitored through time, in selected thermal springs are probably produced by mixing with non-thermal waters. During the summer months at times of maximum flow, selected hot springs exhibit their highest temperatures and maximum enrichments in most chemical constituents (Cole, 1983) .

Hussain, et al. (2009) investigated some of heavy metals ions concentrations in some Iraqi water resources. they found the lowest concentration of the metal ions in the ground water were found in Al-Sulaimaniyah and the highest were found in Dora, Baghdad, for all metal ions except the iron which was the highest in Al- Sulaimaniyah, while the lowest iron concentration was found in Baghdad ground water samples .

In Jordan , several hot springs distributed in different regions having temperature ranges between 20 and 63 have been known by geologists for many year, geographical distribution , chemical and physical characteristics of these springs were described (Harahsheh , 2002; Sunna, 2004; Swarieh, 2000).

Moller et al(2007) found that the changes in the concentrations of major some minor and trace element occurring in both surface and ground water of the lower Jordan river -Dead Sea drainage basin have been investigated in order to identify the characteristics of the regional aquifers and their recharge area.

Salameh and Rimawi(1984) found that the thermal springs mix with fresh ground water at Dead Sea water under a normal geothermal gradient .

Rimawi and Salameh(1988) found that the thermal water discharged in the Zerka Main -Zara area consists of three end members mixed in different ratio with a component of old (many thousands of years) thermal water under saturated in carbonate minerals and containing hundreds of milligrams per liter of free CO_2 .

Tarawneh et al (2000) investigated the water quality of spring in Tafila region and found that the pollution is surface phenomena and not within ground water .

Batayneh (2010) found that the water springs of the Yarmouk basin in the north Jordan are contaminated with heavy metal and the concentration of heavy metal for both seasons are higher than maximum permissible concentration level (MPCL) recommended by Jordan (JISM) (2008) .

The fresh water thermal spring of Zerka Main , were analyzed by Oren . et al (2009) they found that high concentration of major ions such as Na^{+}, K^{+}, Mg^{+2}, Cl^{-} , SO_4^{-2}.

Ground waters in the Mukhebeh wells(in northern Jordan) are low salinity (500 mgl^{-1} TDS) Ca(Mg) - HCO_3 waters with elevated HS^{-} attributed to sulphate reduction driven by oxidation of aquifer-derived

organic matter. The Jordan rift valley(JRV) ground waters are similar to the Mukhebeh waters with the exception of higher Mg^{2+} and HCO_3^- attributed to dolomite dissolution and sulphate reduction. Ground waters from JRV and the Maqla spring at Mukhebeh are NaCl waters with a strong Ca(Mg)-HCO_3 facies (900 to 1000 mg 1^{-1} TDS). The elevated temperatures of all ground waters (30 to 54°C) can be attributed to heating along a local geothermal gradient of 2.5°C per 100 m.(Baijali et al 1997) .

Al-Rawajfeh , et al(2007) investigated the Assessment of tap water resources quality and its potential of scale formation and corrosivity in Tafila province , south Jordan, water sample exhibit high concentration of Cl^-, SO_4^{2-} and HCO_3^- as the major anion and Ca^{2+} and Mg^{2+} as the major cations, Most of the water samples have SO_4^{2-}/ HCO_3^- ratio of less than 1. At least 94% of the scale composition is $CaCO_3$ (aragonite).

Al-Kharabsheh , et al (2003) investigated the effect of urbanization, drought and pollution on the deterioration of water quality in the Tafila Basin in southern Jordan during the year 2000. Six representative springs were chosen, from which 84 water samples were analyzed for their chemical and biological characteristics. The primary evaluated parameters are EC, NO_3, Their concentration is accelerating, due to the increase of waste water in comparison to fresh water quantity. The fracture system associated with Upper Cretaceous carbonates allows the waste water to recharge the springs very quickly and without any purification.

The soil might be contaminated by heavy metal such as Fe, Cu ,Mn ,Cr ,Ni, Zn, heavy metal presented in the seriously contaminated agriculture rice soil in the Gunda plain, northern Taiwan, the results showed that higher concentration of heavy metal showed in the 60-80and 80-100cm layer, the Contamination of soil due to irrigation by thermal water during drought seasons[Chiang et al 2010].

The mean concentrations (ppm) of heavy metal such as Cu, Zn in urban soils (0-10cm) are: 73,183, respectively (Thornton 1991).

The uptake and bioaccumulation of heavy metals in vegetables are influenced by a number of factors such as climate, atmospheric depositions, the concentrations of heavy metals in soil, the nature of soil on which the vegetables are grown and the degree of maturity of the plants at the time of harvest (Lake et al., 1984), (Scott et al., 1996) and (Voutsa et al., 1996)

Anthropogenic it is main sources of heavy metals include the addition of manures, sewage sludge, fertilizers and pesticides, which may affect the uptake of heavy metals by modifying the physico-chemical properties of the soil such as pH, organic matter and bioavailability of heavy metals in the soil. Whatmuff (2002) and McBride (2003) found that increasing concentrations of heavy metals in soil increased the crop uptake.

Assessment of heavy metal content in lichens and soil samples from various localities of Hosur Road , Bangalore south India was under taken ,

top soil sample (0-10 cm) were taken at various locations, the metals analyzed were Cr ,Pb, Fe, Zn, Ni and Cu, the geoaccumulation index of these metal in the soils, under study residential areas indicated that they are uncontaminated with Ni,Zn and Fe and moderately contaminated with Cr and Pb, in industrial areas and traffic junctions the concentration of Fe, Pb and Ni was maximum (Begum et al, 2009).

High concentration of heavy metal such as (Zn , Cr , Pb , Cd ,) in soils of central Jordan (Fuheis from parks) are related to anthropogenic source such as cement industry ,fertilizer , and vehicle exhausts (Banat et al 2005).

In southern Jordan around the cement factory , the results showed high concentration in urban soils (0-10cm)of Pb and Zn reached to 55 , 44.52 ppm , respectively, and concentration of Cu and Cr reach to 2.89, 22.18ppm (Al-Khashman et al, 2007).

In a study conducted by Al-Zu'bi (2007), the concentration of heavy metal such as (Fe , Cr , Cu , Zn , Ni) in soil in Jordan valley irrigated by different water qualities (fresh water from the Yarmouk river and the other irrigated with treated waste water from King Talal Dam), the result indicate that all of the heavy metals were present at concentrations compared with the optimum concentration that were within the accepted limits.

Calcite predominated in the central region whereas calcite and quartz are the dominant minerals in south Jordan. The concentrations of Hg, Cr, Ni, Cu, Pb and Zn were higher in central Jordan, which might be attributed to higher anthropogenic activities than south. On the other hand, Fe, Mn, Ti, Ba, Sr, Y and Rb were higher in the south of Jordan reflecting the composition of soil at these sites. At Aqaba city, the only port of Jordan, Cr, Cd, As and S were higher than other areas, This variation might be attributed to the contribution of phosphate dust in the atmosphere through handling processes (Jiries et al 2002).

Chapter Three
Material and Methods

All chemicals and reagent used in analysis of samples supplied from Charlau and Hach companies. In order to achieve the aims of this work chemical analysis of Afra and Burbeita thermal spring waters and soils irrigated with the effluent of these streams was investigated for major ionic composition (HCO_3^-,Cl^-, NO_3^-, SO_4^{-2},Ca^{+2}, Mg^{+2}, Na^+ and K^+) for water samples and six heavy metals (Fe, Zn, Cu, Co, Cr and Ni) for both soil and water samples. Detailed description of the procedures and analysis are given below.

3.1 Sample collection

1. Water sampling

All springs issued from Afra (figure 2) and Burbeita (figure 3) were collected at two periods once during February and march 2012 representing the end of winter season and once during August 2012 representing the end of the summer season.

In Afra site the water issues from six springs which were sampled in addition to the effluent from all sites where its water is used to irrigate farms located downstream. For Burbeita site the water is issued from only two sites.

Sampling for each site was done for all sites in two PVC bottles one for major ionic composition using 1L PVC bottles washed three times with the sample water before being collected .

For heavy metals sampling, 250ml PVC bottles were used after being washed with 10% nitric acid and washed several times with sample water before sampling. To each bottle few drops of concentrated nitric acid were added to eliminate precipitation of heavy metals during transportation.

The collected water samples were transferred to the laboratories of "Jordan Abyad Fertilizers and Chemicals Company and analyzed on the same day of sampling to avoid any change in its composition.

2. Soil sampling

Soil sampling was carried out once at the end of the winter season from two sites located downstream from Afra and Burbeita thermal water where the source of irrigation water is the effluent water discharge from the thermal springs, in addition to a site where no irrigation is practiced and considered as a blank sample.

Soil sampling for each location was done from two depths, upper soil (0-10 cm depth) and lower soils (10-20 cm depth). All sampling was done in triplicate from each sampling location to ensure reliability of the results

and transferred to the laboratory at Mutah University for sample digestion and preparation.

3.2 Sample Preparation

After collection, Each soil sample was oven- dried at 105^oC until constant weight was achieved indicating removal of the soil moisture. After drying each sample was sieved through 2mm stainless mesh to remove large particles and plant remains from the soil.

For each soil samples , 1 to 2 grams of soil was accurately weighed and placed in test tube , 10 mL concentrated nitric acid were added and sonicited for one hour at 90^oC (Hewitt et al ,1990) . The samples were left to cool and contents were filtered through Whatman filter paper No.42. Each sample solution was made up to a final volume of 25 ml using 1% nitric acid and polyethylene volumetric flasks. and stored at 5^oC until analysis for heavy metals analysis which was done within few days.

3.3 Analysis

Each of the collected water samples were analyzed for it physical parameters (Electrical conductivity (EC), pH and Temperature), Major anionic composition (HCO_3^-, Cl^-, NO_3^-, SO_4^{-2}) and cationic composition (Ca^{+2}, Mg^{+2}, Na^+ and K^+). For all samples heavy metals concentrations (Cr, Cu, Fe, Ni, Co and Zn) were determined. Detailed description of the analysis is as follows:

1. Physical Parameters (Temperature, EC, and pH).

Measurements of Temperature, EC and pH were done on site to prevent any alteration of these parameters during transport . Temperature and EC it were determined using WTW conductivity meter (LF 320), pH measurements was done using pH meter supplied from (WTW/Germany).

2. Major ionic composition

Major anions (Cl^-, NO_3^-,$HCO_3^-$and SO_4^{-2}), and major cations (Ca^{+2}, Mg^{+2}, Na^+ and K^+) were determined for all collected water samples. All samples were stored at 5^oC and analyzed within 48 hours after sampling by using the following methods.

3.4 Cations analysis

1. Magnesium, Calcium and Total Hardness

Magnesium

Determination of Magnesium (Mg), Calcium (Ca) and Total hardness (TH) was done by complex with EDTA Di-sodium salt (0.0588 M). Mg and T.H are simultaneously titrated. Using Manver indicator (tri-ethanolamine) as masking agent suppresses interference from most metal ion, and suitable indicator. By precipitating magnesium with potassium hydroxide, Calcium can be independently titrated. Magnesium is

determined from the difference of two titrations (Official method AOAC , 2010).

Calcium

Twenty ml of water sample was transferred in 250 ml Erlenmeyer flask, few drops of NaOH was added to bring the pH of solution to 12.2, 0.1 gm Calver indicator (Hydroxynaphthol blue) and 50 ml de-ionized water (Color is pink) were added to the water sample. The solution was titrated with EDTA Di-sodium salt solution where the end point was marked by changing the color from pink to dark violet. The volume of titrant (V2) was used to calculate the calcium concentration (Official method AOAC , 2010).

Total hardness (TH)

Twenty ml of the sample was transferred into 250 ml Erlenmeyer flask, 10.0 mL Ammonia Buffer solution pH= 10 was added and it was checked for pH. Manver indicator (0.1 g) and 50 mL de-ionized water was added and shake (color is red). Titration against EDTA Di-sodium salt was done until endpoint was reached which was marked by changing the color from red to dark blue. The volume of titrant (V1) was used to calculate the Total Hardness concentration, V2 used to estimate of the Ca concentration(Official method AOAC, 2010). Calculation was done to evaluate the concentration in ppm of Ca, Mg and Total Hardness as follows:

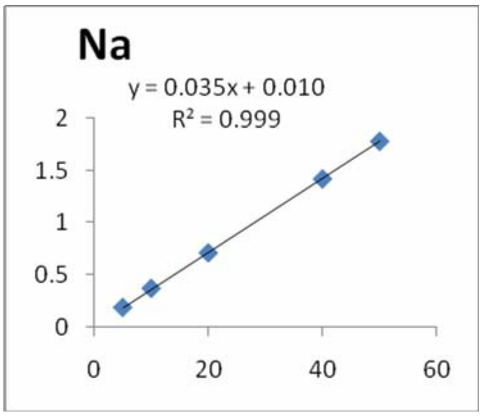
Ca (ppm) = (V2*(M) EDTA*40.09*1000) / Sample volume

Mg (ppm) = [(V1-V2) * (M) EDTA* 24.3* 1000] / sample volume

TH (ppm)as$CaCO_3$ =[(V1) *(M) EDTA * 100 * 1000] / Sample volume

2.Sodium and Potassium

Sodium and potassium were analyzed by using atomic absorption spectrophotometer (Varian AA 240FS), using their standards solution shown in figure 4.



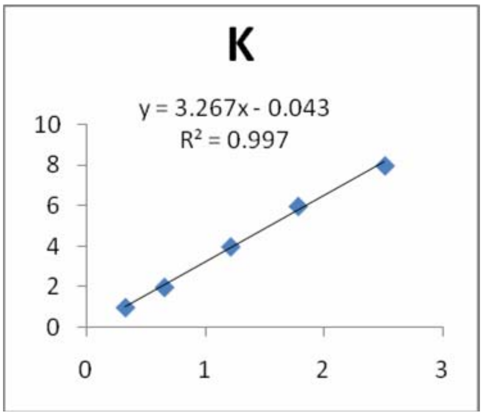


Figure 4
Calibration curve for Na and K Where the X-axis is concentration and Y-axis is Absorbance

3.5 Anions Analysis

1.Chloride

To estimation the Cl^- concentration, titration method was used with silver nitrate and using Ion Selective Electrode (ISE) to detect the end point.-

Ten ml of the water samples were transferred into 250 ml beaker with Ten ml of 2 N HNO_3. The electrode was rinsed with de-ionized water and wiped with soft clean paper. The electrode was immersed in the sample. Titration was done with $AgNO_3$ using (848 Titrino plus, Metrohm, Swiss) equipment to detect the end point. For blank , 100 ml of de-ionized water mixed with 10 ml concentrated HNO_3 was used(Annual book of ASTM , D512-04 , 2009). for chloride calculation the following equations were used . Cl^- (ppm) = [(A-B)× N× 35.453×1000] / sample volume .

N ($AgNO_3$) = 0.0853 , M.wt (Cl) = 35.453

A= ml titration of sample. B= ml titration of blank.

2.Sulfate

Concentration of sulfate was determined by gravimetric method by using Barium chloride solution reacts with sulfate under acid conditions, giving white precipitate of Barium sulfate (Official method of analysis of AOAC , 2005).

One hundred ml sample was filtrated and transferred into 250ml beaker, Ten ml of 6N HCl was added and heated with stirring for few minutes, then 20 ml of $BaCl_2$ was added and heated using hot plate in vacuum hood for 1 hour. The solution was left for two hours to precipitate. the sample was shaken and filtrated. The precipitate was dried by oven at 150^oC for 30 minutes and weighted.

Concentration of sulfate was estimated using the following calculation

SO_4^{-2}(ppm) = [(weight of dry precipitate $BaSO_4$) / sample volume] ×411.6

*(Mwt(SO_4)/Mwt($BaSO_4$)=0.4116)

3.Bicarbonate

Bicarbonate was determined by titration method. One hundred ml of water sample was transferred into 250 ml Erlenmeyer flask. Few drops (3-5 drop) of phenolphthalein indicator was added and titrated with 0.10 N HCl. The end point was marked by changing the color from violet to colorless (V1), 3-5 drop Bromocresol green indicator was added and titration continued while change the color change from blue to yellow (V2) . In all sample V1equal zero, that mean all samples contain just bicarbonate (Annual book of ASTM , method D3875, 2009).

The volume of titrant (V2) was used for calculation of bicarbonate concentration using the following equation

V2*N(HCl)*50*1000/ (ml of sample)= T-alkalinity [mg/l as $CaCO_3$]

Where (N=Normality , 50=Equivalent Wt for $CaCO_3$)

4.Nitrate

Nitrate were determined by spectrophotometric method using UV-Visible Spectrophotometer (at 220 nm) supplied from Libra 580 biochrom England. figure 5 shown their calibration curve for Nitrate .

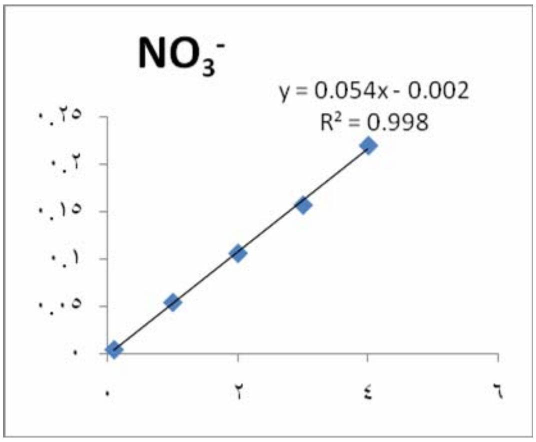


Figure 5
calibration curve for Nitrate (NO_3^-)

3.6. Heavy metals

Zinc (λ=213.8), Nickel (λ=232), Copper (λ=324.8), Iron (λ=248.3), Chromium (λ=357.9), and cobalt (λ=242.5nm) were determined by using Fast Sequential atomic absorption spectrometer supplied from Varian (AA240FS) , using (Air-C_2H_2), sensitivity (0.1-20mg/l).

Standard solutions for (Zn , Ni , Cu , Fe , Cr , Co,) were prepared by dilution of stock solutions and calibration curves were drawn using their standards solution as shown in figure 6 .

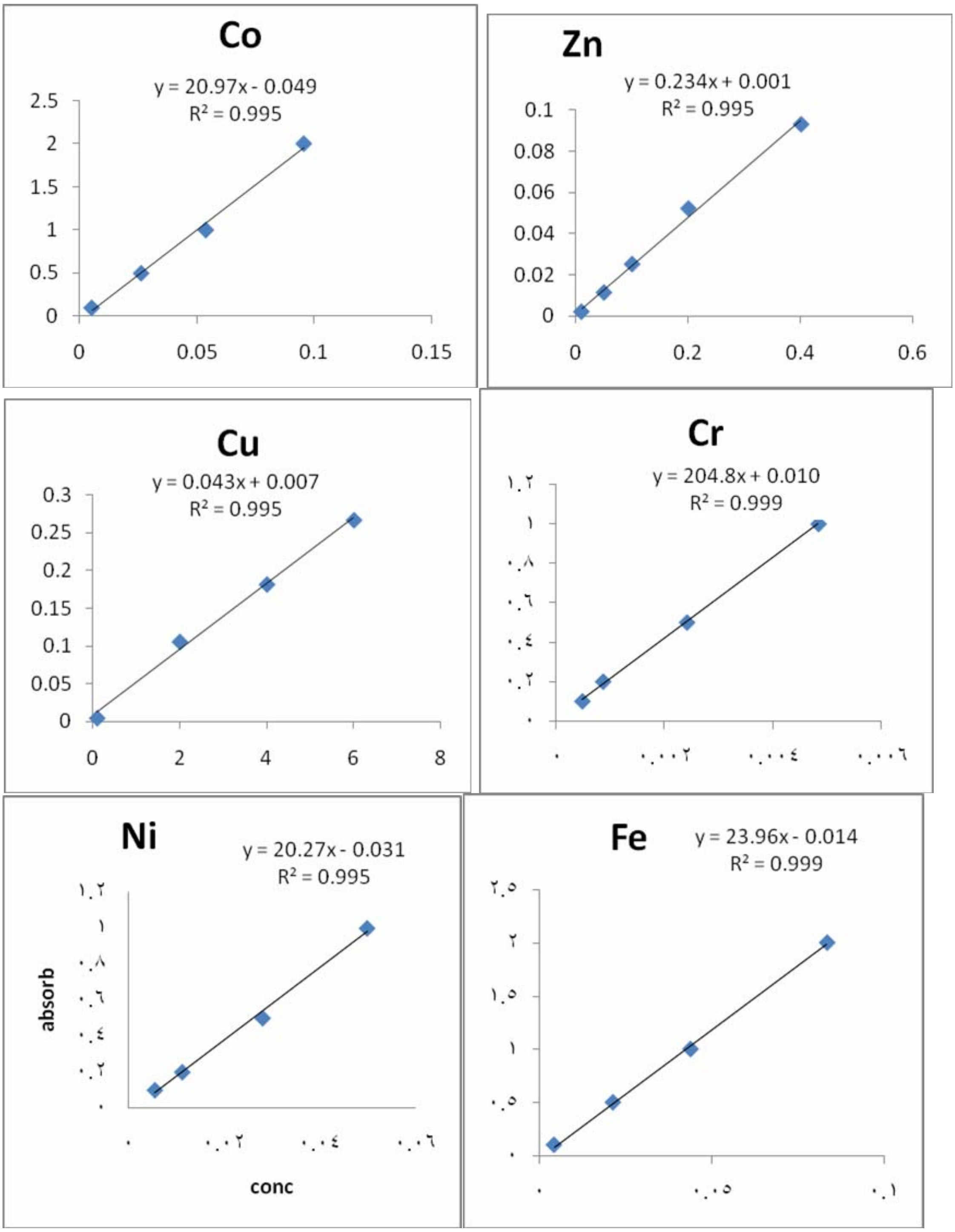


Figure 6

Calibration curve for heavy metals(Co, Zn , Cr ,Cu , Fe , Ni) Where the X-axis is concentration and Y-axis is Absorbance.

Chapter Four
Results and Discussion

Although quantities of water is very important in Jordan due to its location in an arid to semi arid environment, the water quality is of equal importance to the water quantity.

Many factors influence the water chemistry of springs such as the chemical composition of the aquifer, temperature, solubility of the minerals and the length of time that water is in contact with those materials.

The hydro chemical study for two thermal springs (Afra and Burbeita) at Tafila region was done through investigating the major, minor and trace ionic concentrations. Besides, these ionic concentration, the study also involves the salinity (total dissolved solids TDS), electrical conductivity (EC) and acidity (pH). In addition to heavy metals in soil irrigated with the thermal water. Some of the chemical parameters such as electrical conductivity, pH and temperature can change rapidly once a sample is extracted from a well and exposed to light, air, or other environmental factors (Sanders, 1998) therefore it was measured immediately on site after sampling to avoid any changes due to transferring the samples to the laboratory.

The water samples were collected from six springs at each site in two periods, the first sampling campaign was done at the end of winter season 2011-2012 during February and march 2011 representing the wet season and the other sampling campaign was done during July and August 2012 representing the end of the dry period.

4.1. Accuracy of the results

The accuracy of the results of the water samples analyses can be estimated using the ion balance (*IB*) equation.

By calculation absolute difference between total of cations and anions concentration on total for these concentrations in (eq/l) units as percentage and according to the following equation

$$IB = \frac{|\text{sum of cations} - \text{sum of anions}|}{|\text{sum of cations} + \text{sum of anions}|} \times 100$$

where cations and anions are expressed in meq/L.

When (IB≤5%)(certain) the results could be accepted for interpretation, but if (5%≤IB ≤10%) (probable certain) the results are acceptable with risk , but if the value (IB > 10%) (uncertain) cannot depended on the results in hydro chemical interpretation . The IB values of all analyzed samples were less than 4%. Therefore the results of the analysis can be used in the hydro chemical interpretation for the study area.

4.2. Afra springs

Summary of the physical parameters (Electrical conductivity, temperature and pH) as well as major ionic composition (HCO_3^-, Cl^-, SO_4^{-2}, NO_3^- , Ca^{+2}, Mg^{+2}, Na^+ and K^+) of Afra springs and for the two periods (end of winter and end of summer season) are given in tables 1 and 2, Discussion of each parameter is given below.

4.3.Physical Parameters

1.Temperature

As shown in tables (1) and (2)the temperature of the thermal springs ranged from 33.3 to 46.3 ˚C with an average temperature of 40.1 ˚C at the end of the winter season and from 35.7˚C to 47.2 ˚C with an average temperature of 42.5 ˚C at the end of the summer season. This slight increase of temperature at the end of summer season (Figure 7) can be attributed to present environmental temperature.

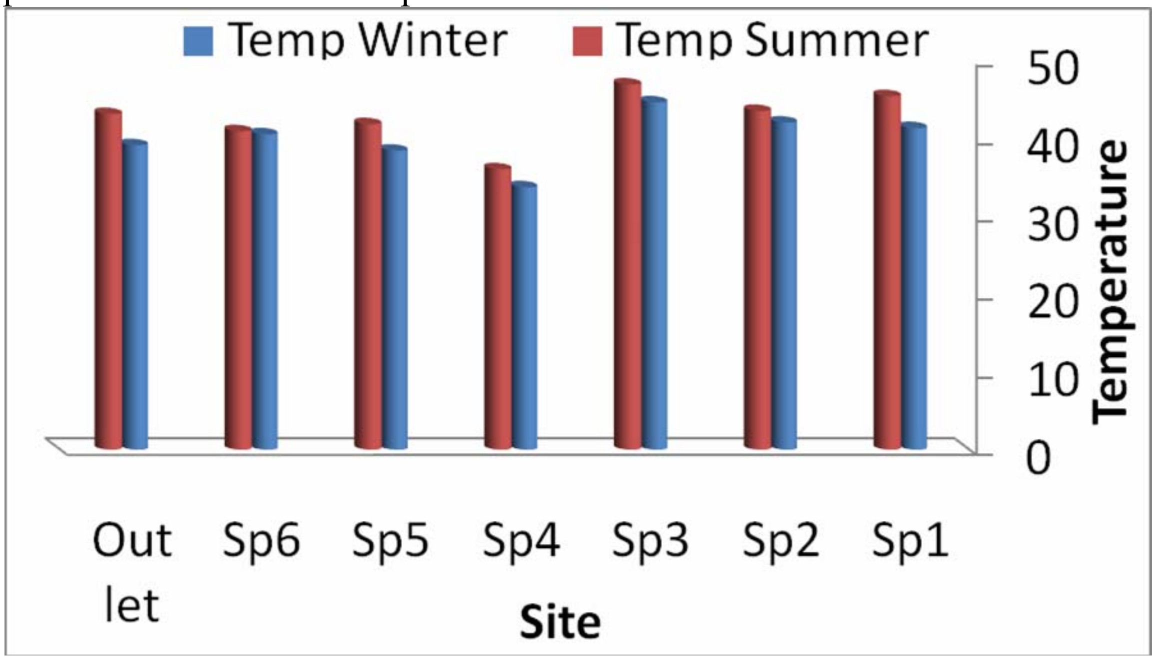


Figure 7

The average of temperature at Afra site in both winter and summer season.

2. pH

The pH value is a measure of acidity or alkalinity of water (Langmuir, 1997) which plays an important role in the water chemistry especially the carbonate rocks which easily dissolve under acidic conditions. The dissolution and mobility of metals in natural water are greatly influenced by the (pH) (Thompson et al.,2007).

As shown in Tables (1) and (2) the pH values of water collected from different locations at Afra sites were near to neutral condition due to buffering effect action of dissolved minerals especially carbonate rocks of

the aquifers where it ranged from 7.0 to 7.57 with an average value of 7.17 in winter season and from 7.09 to 7.58 with an average value of 7.30 during summer season.

At both seasons the highest pH was observed at the outlet Figure (8). The trend of increasing alkalinity of water at the outlet which can be explained by the release of CO_2 during flowing of the thermal water from the springs to the outlet.

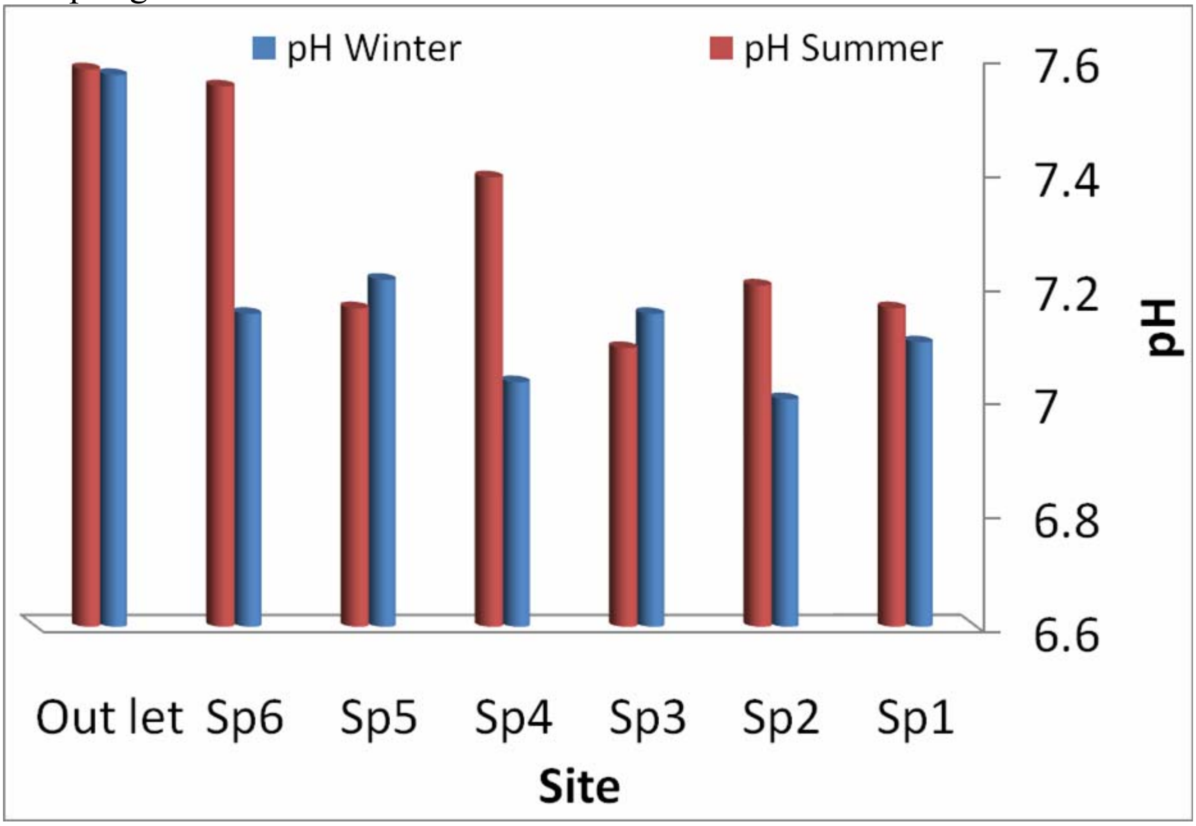


Figure 8
pH value for different sites in Afra at winter and summer season.

3. Electrical Conductivity

Electrical conductivity reflects the capacity of water to conduct electrical current, and is directly related to the concentration of salts dissolved in water. The EC depends on water temperature, where an increase in water temperature by one degree Celsius causes an increase in electrical conductivity by (2%) (Hem, 1985).

As shown in tables (1) and (2) the electrical conductivity of the springs at Afra ranged from 508 to 567.6 µS/cm with an average value of 552.2 µS/cm during winter season and from 494.0 to 570 µS/cm with an average value of 557.8 µS/cm.

As shown in figure (9) the electrical conductivity of the thermal water in both the seasons were very close to each other indicating that the rainy season do not play an important role in the water salinity.

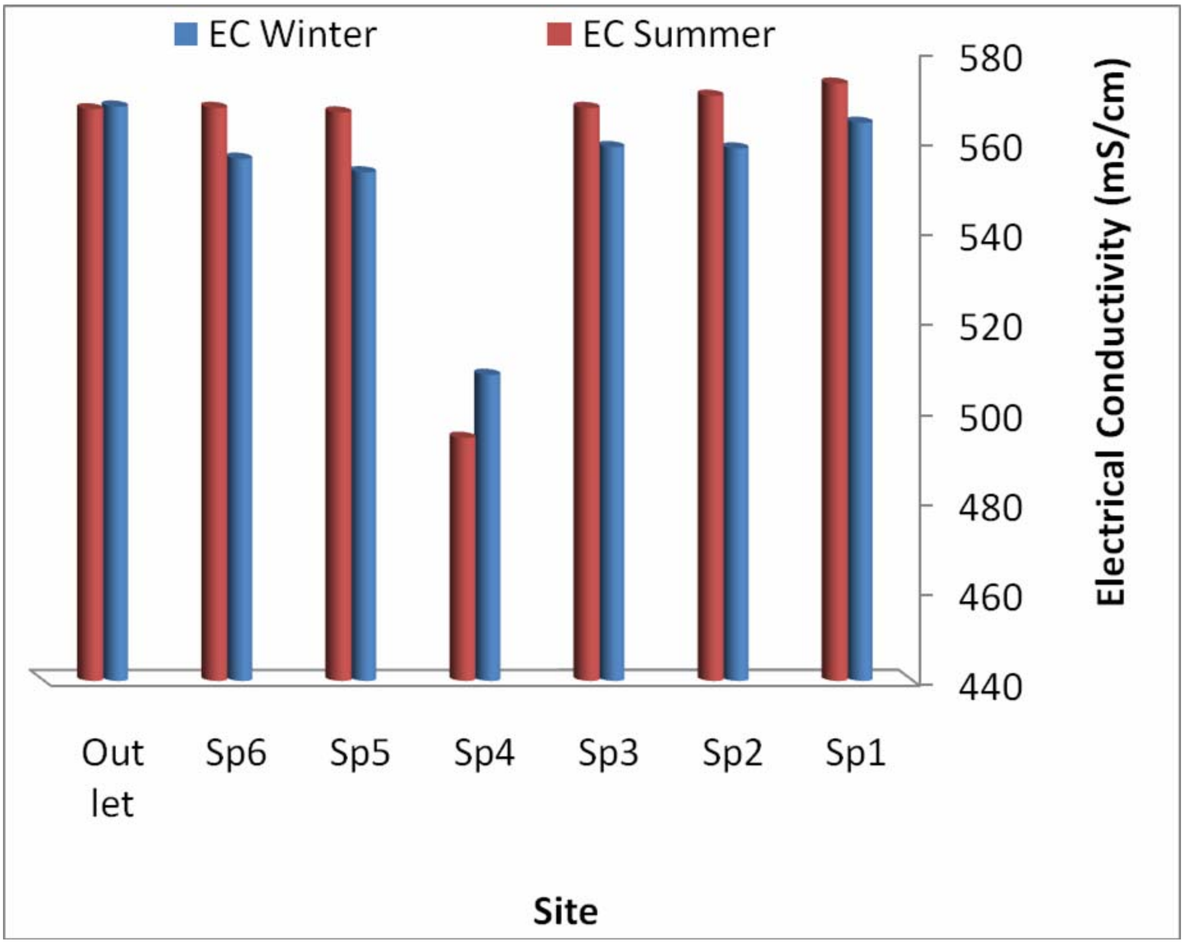


Figure 9
Electrical conductivity at Afra site in both winter and summer season.

4.4. Chemical Parameters
1. Major Cations
Water Hardness

Hardness is measurement used originally to investigate the suitability of water for washing with soap .In hot springs water , when water passes through or over deposits such as limestone, the levels of $Ca^{2+}$and Mg^{2+} ions present in the water can greatly increase and cause the water to be classified as hard water, the United State Geological Survey uses the following classification of hard and soft water : (0-17.1) soft , (17.2-60) slightly hard ,(60-120)moderately hard , (120-180) hard , and (Above 180) Very Hard .

Calcium

Calcium is an essential constituent of sedimentary rocks, and it results from the erosion of igneous and metamorphic rocks. Calcium is the most abundant element of the alkaline -earth metals, and is an essential element for plant and animal.

The flow of groundwater through rock bodies such as limestone, dolomite and gypsum which cover most of the study area and solution of

carbonates and gypsum can explain the concentration of anions and cations in the geothermal waters of the study area

As shown in Tables (1) and (2), Ca concentration ranged from 33.9 to 76.6 ppm with an average concentration of 52.0 ppm at the end of winter season and from 44.78 to 84.82 ppm at the end of summer season.

Figure (10) shows the concentration of Ca ions at different location within Afra site. It is clear that that there was no significant changes in Ca concentrations between summer and winter season for the springs water but it was clear at the outlet which showed a significant increase in Ca concentrations at the end of summer season which can be due to evaporation of the thermal water during hot and dry summer conditions increased with the high temperature of the thermal water

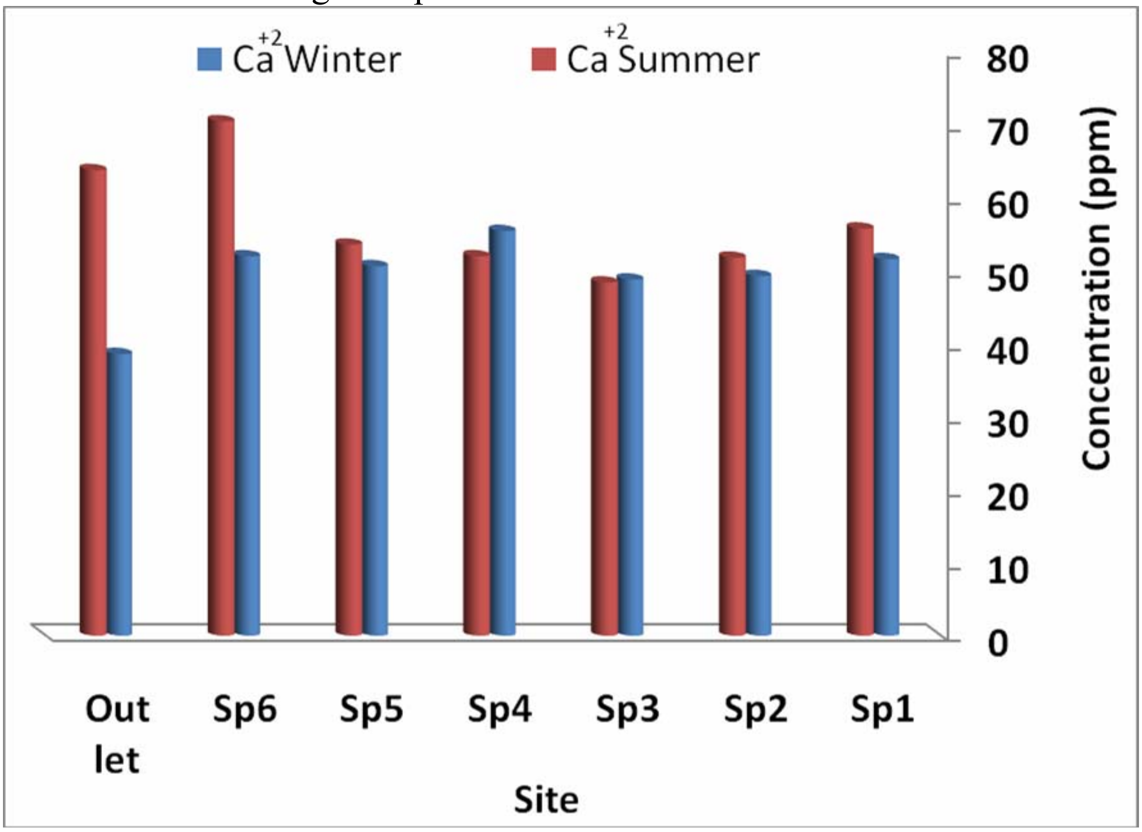


Figure 10

Concentration (ppm) of Calcium in water from Afra site in both winter and summer season.

Magnesium

Magnesium is a common ion in the water resources in Jordan which is due to the carbonate composition of the aquifers. The flow of groundwater through rock bodies such as limestone, dolomite and gypsum which cover most of the study area and solution of carbonates and gypsum can explain the concentration of anions and cations in the geothermal waters of the study area.

As shown in tables (1) and (2), the concentrations of Mg during winter season ranged from 14.6 to 20.7 ppm with an average concentration of 17.4

ppm. In dry summer season it ranged from 5.72 to 30 ppm with an average value of 20.1 ppm.

Figure (11) showed the concentrations of Mg for two seasons at different locations. It is clear that there was a slight increase at the end of summer season which can be explained as the same mechanism of increasing Ca due to evaporation effect.

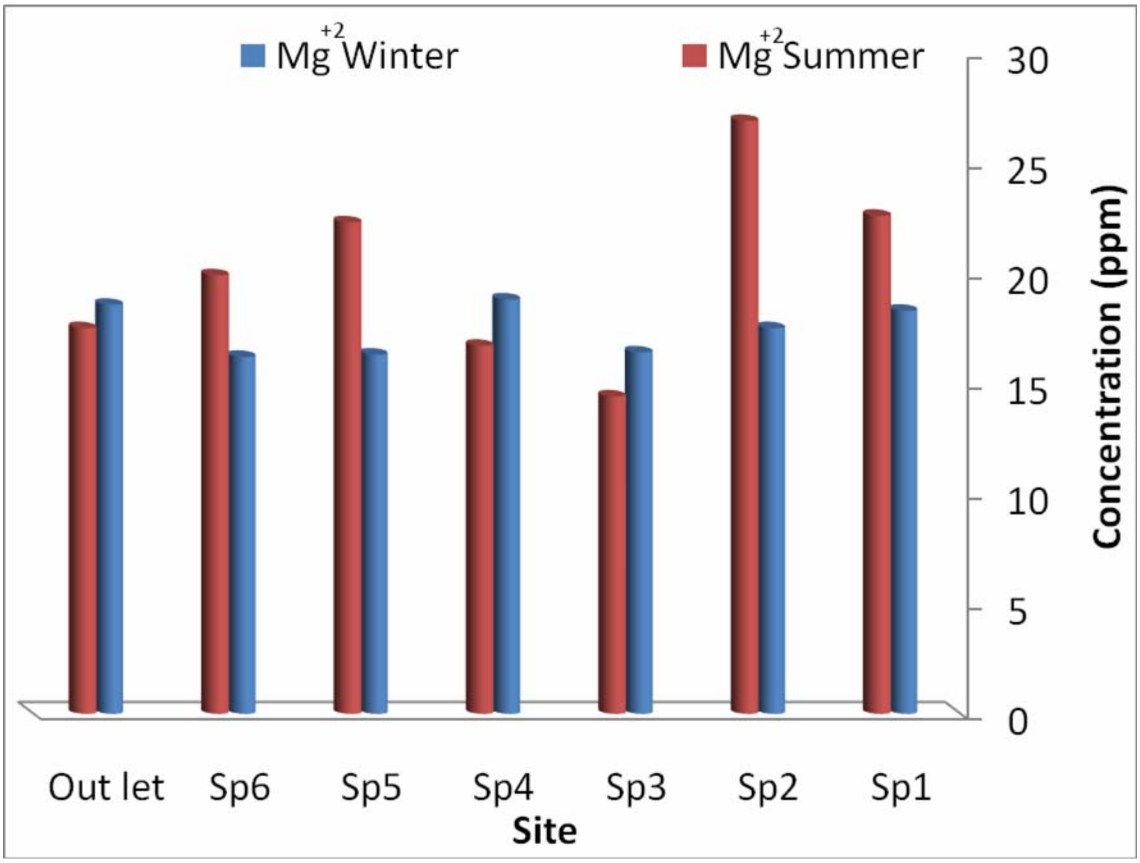


Figure 11
concentration (ppm) of magnesium in water from Afra site at winter and summer season.

Sodium

Although sodium is a common ion in water resources in Jordan due to its semi arid climatic conditions. Most of salts and sodium compounds have high solubility in water , the most soluble salt among them is sodium chloride (NaCl) while the least is sodium bicarbonate ($NaHCO_3$); their solubility increases normally at high temperatures (Hem,1985).

The concentrations of sodium was relatively low in the thermal springs of Afra Tables (1) and (2) as it ranged from 32.5 to 35.0 ppm with an average value of 34.0 at the end of winter season and it ranged from 31.1 to 35.1 ppm with an average concentration of 33.4 ppm at the end of the summer season. Figure (12) shows the average concentration of sodium at different sites at Afra during both winter and summer seasons. It is clear

that the seasonal variation did not play an important role in the concentration of sodium indicating that the path of water of groundwater flow did not cross sodium rich layers.

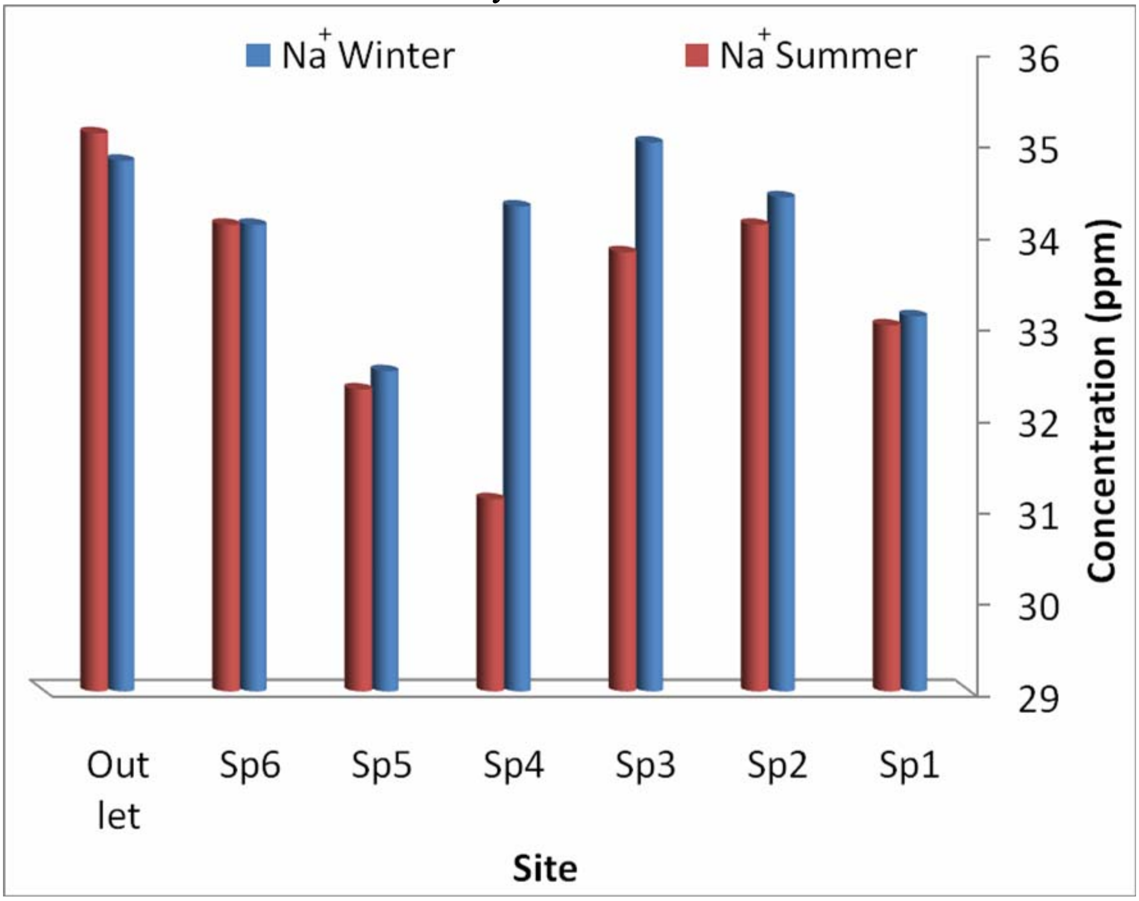


Figure 12

concentration (ppm) of sodium in water from Afra site at winter and summer season.

Potassium

Potassium is common ion in silicate minerals such as orthoclase, microcline, hornblende, muscovite and biotite in igneous and metamorphic rocks and evaporate deposits gypsum and sulphate release considerable amount of potassium in to groundwater through weathering.

The concentration of (K^+) in all sample in Afra shows in Tables (1) and (2) where it ranged from 2.29 to 2.96 ppm with an average concentration of in Sp1 (rainy season), and 2.28 to 3ppm in Sp1 (dry season)

Potassium concentration in to hot springs water in all samples was relatively low as one of the main sources of potassium in groundwater is the agricultural activities (Sayyed. A. and Bhosle . B, 2011) which is scarce at the recharge area of these springs.

Figure (13) shows the average concentration of potassium at different sites at Afra at the end of both winter and summer seasons. It is clear that

the concentrations were very close to each other indicating no variation with different seasons.

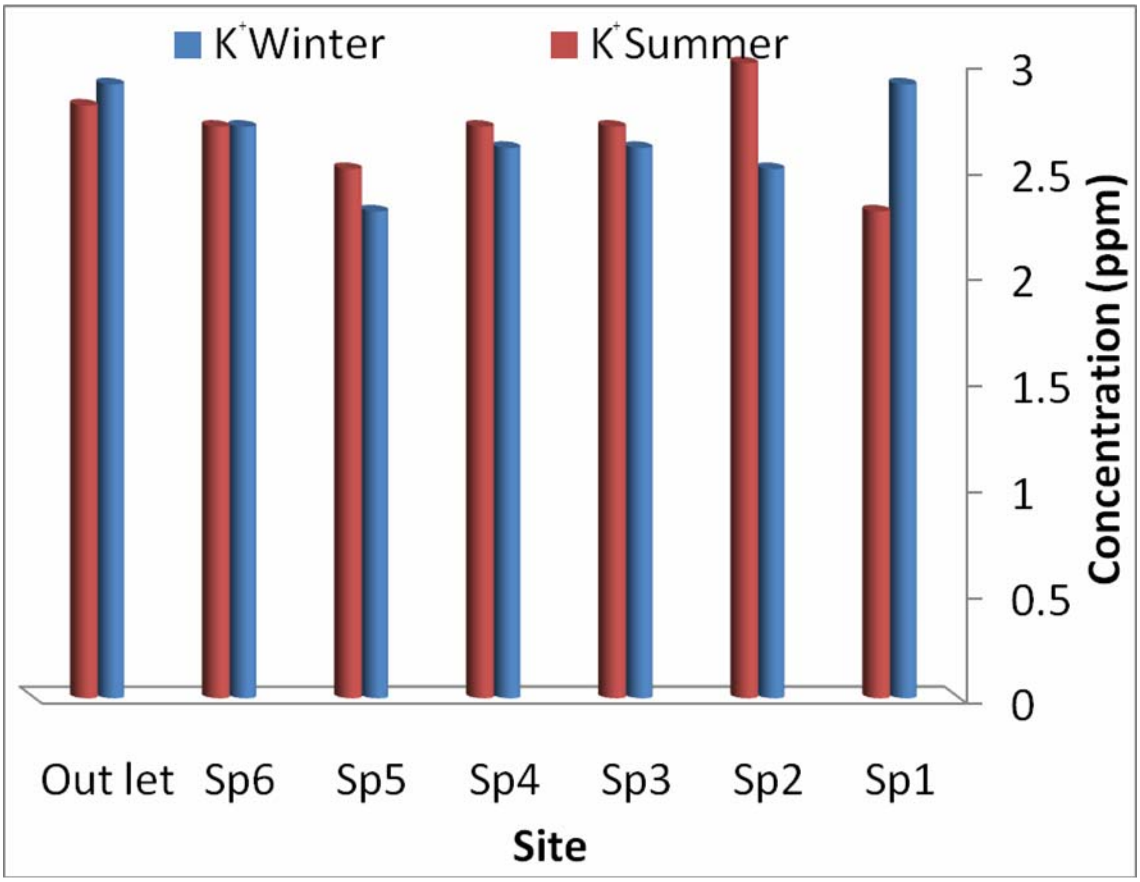


Figure 13

concentration (ppm) of potassium in water from Afra site at winter and summer season.

2.Major Anions

Bicarbonates (HCO_3^-)

Bicarbonates are one of the most abundant groups in the fresh water in Jordan as most of the aquifers are composed of carbonates.

The concentrations of HCO_3^- was in its normal range in the thermal springs of Afra tables (1) and (2) as it ranged from 84.4 to 128.3 ppm with an average value of 101.9 at the end of winter season and it ranged from 78.7 to 110.7 ppm with an average concentration of 100.8 ppm at the end of the summer season.

As shown in figure (14) there was a slight variation in HCO_3^- concentrations between summer and winter seasons and it was slightly higher in winter seasons than in summer season which can be explained due to the recharge occurrence which coincides with the values of (pH).

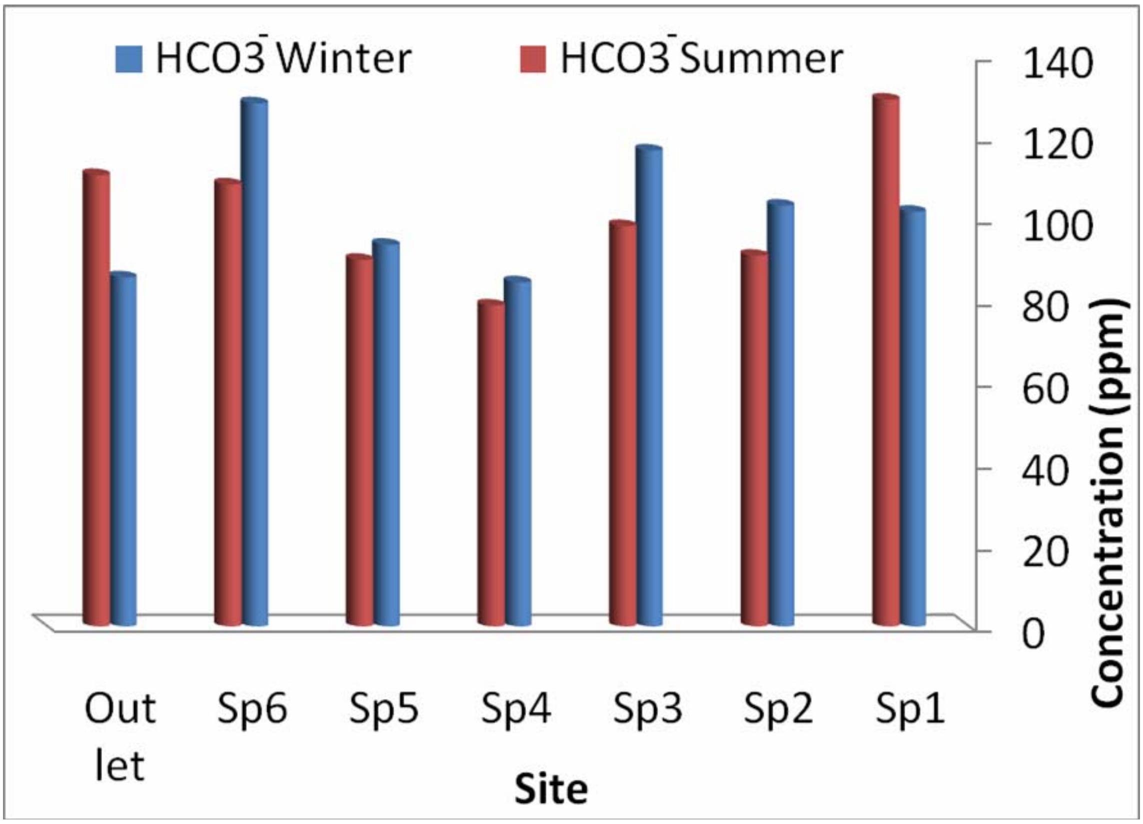


Figure 14
concentration (ppm) of bicarbonate in water from Afra site at winter and summer season.

Chloride

Although chloride is a minor element in the earth crust it occurs in almost all natural waters due to its high solubility chloride is harmful for plants when it occurs at high concentrations where some damage may occur at level as 70-250 ppm (Radojevic and Bashkin 2006 , 2nd Edition) .

As shown in figure (15) there was an increase in Chloride concentration during summer season where the most probable source is the sweat of the bathers using Afra spring for medical purposes where such activity is higher during the summer time than cold winter season and in all thermal water of the investigated area.

The chloride concentration for different springs in Afra ranged from 50.5 to 130 ppm with an average concentrations of 79.9 ppm at the end of the winter season) whereas it ranged from 107 to 140 ppm with an average value of 120.7 ppm at the end of the summer season. Generally, an increase of chloride concentrations was observed with increasing temperature.

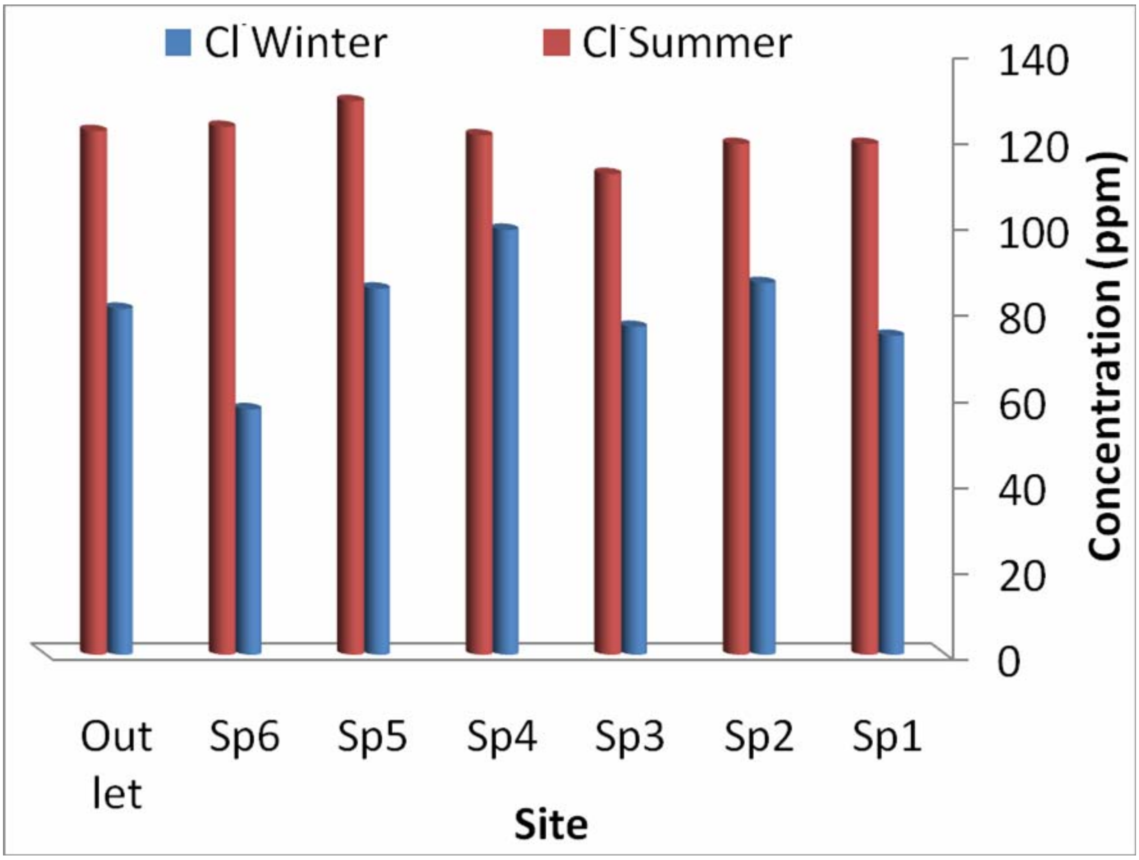


Figure 15
concentration (ppm) of chloride in water from Afra site at winter and summer season.

Sulfates

Sulfates are widely distributed in nature and may be present in natural water and may present in concentrations ranging from few to several hundred mg/l (Radojevic and Bashkin 2006 , 2nd Edition) .

As shown in Tables (1) and (2), the sulfate concentrations ranged from an average of 59.1 ppm to 9.6 ppm with an average concentration of 80.5 ppm at the end of winter season where it decreased at the end of the summer season to concentrations ranging from 46.4 to 74.6 ppm with an average concentration of 63.7 ppm

The seasonal variation of each sampling site is shown graphically in figure (16) where it shows that at the end of the summer season there was a decrease in sulfate concentration in most of the site.

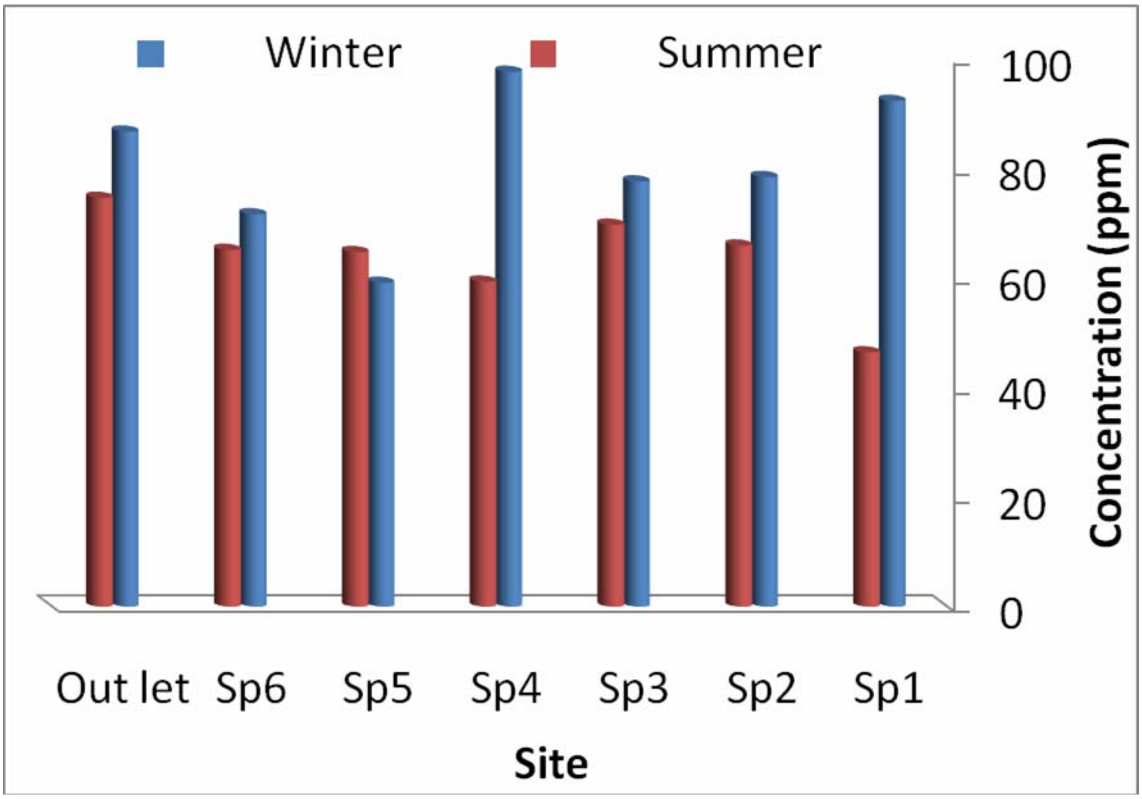


Figure 16
concentration (ppm) of Sulfates (SO_4^{-2}) in water from Afra site at winter and summer season.

Nitrate

Nitrate occurred in very low concentrations in all samples collected from Afra area as shown in tables (1) and (2). The nitrate concentrations ranged from 0.01 ppm to 0.2 ppm with an average value of 0.1 ppm at the end of winter season and from 0.03 to 0.4 ppm with an average value of 0.2 ppm at the end of summer season. The low nitrate concentrations indicate that there is no source of pollution to these springs where the agricultural activities are downstream and did not have any impact on the springs water quality, the results showed variation in concentration of nitrate in different sites from Afra area in both season .

4.5. Burbeita Springs

Burbeita area consist tow springs one of them (Spring No1) it is cold water it used for dinking and irrigation of croups , and other it is hot water. Summary of the physical parameters (Electrical conductivity, temperature and pH) as well as major ionic composition (HCO_3^-, Cl^-, SO_4^{-2}, NO_3^- , Ca^{+2}, Mg^{+2}, Na^+ and K^+) of Burbeita spring and for the two periods (end of winter and end of summer season) are given in Table 3, Discussion of each parameter is given below.

1. Physical Parameters

Temperature

As show in Table (3) the temperature of the thermal springs , In spring (BR1) was ranged from 27..7 to 28.7 ◦C with an average temperature of 28.2 ◦C at the end of the winter season, but in spring (BR2) Temperature ranged from 41.4 to 42.8^{o}C with an average 41.9^{o}C in same season . In summer season Temperature was ranged from 28.8 to 31^{o}C in spring (BR1) with an average 29.9^{o}C , and from 42◦C to 44.3 ◦C with an average of 43.1 ◦C in spring (BR2) at the end of the summer season. the results showed slight increase of temperature at the end of summer season, Figure(17) can be attributed to present environmental temperature.

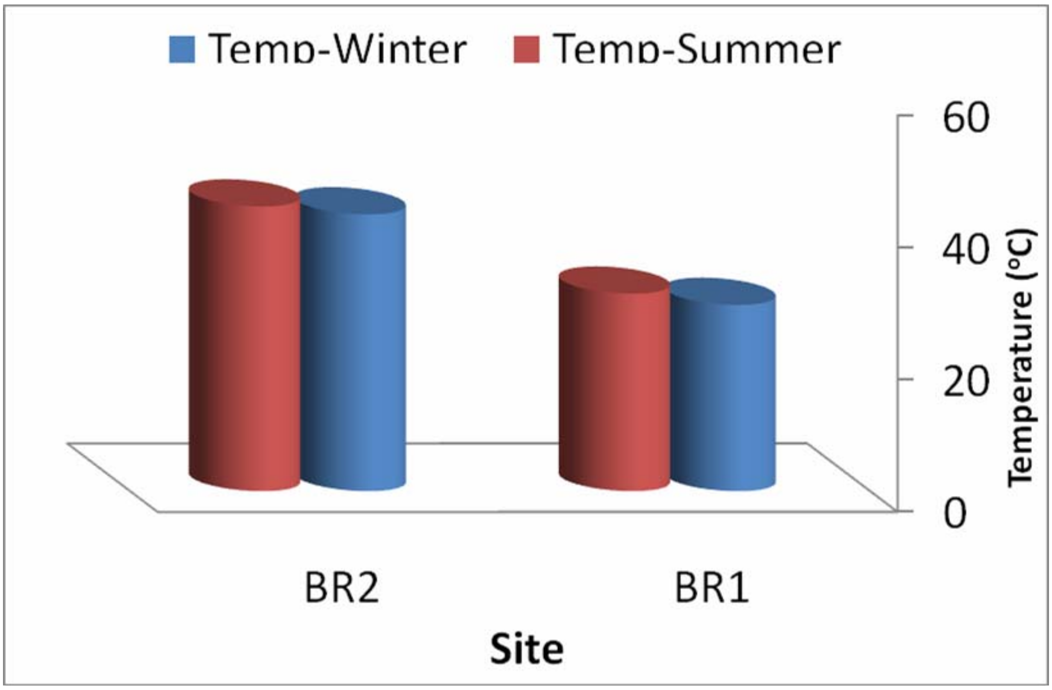


Figure 17

Average temperature in water from Burbeita site at winter and summer season.

pH

As shows in table (3) the pH values of water collected from Two locations at Burbeita sites were near to neutral condition due to buffering effect action of dissolved minerals especially carbonate rocks of the aquifers ,pH ranged from 7.12 to 7.25with an average value of 7.19 in winter season at Spring No1 , and from 6.68 to 7.33 with an average value of 7.01 during summer season , Spring No2 the acidity ranged from 6.5 to 6.76 with an average value of 6.62 at end winter season , in summer season pH ranged from 6.57 to 7.4 with an average value 7.12 at spring (BR2), the result showed that the hot water from spring (BR2) more acidic and the pH at spring (BR2) more effected by temperature than spring (BR1) .

At both seasons the highest pH was observed at the spring (BR1) The trend of increasing alkalinity of water at the spring (BR1).

The pH values of the Burbeita hot water vary between 6.68 and 7.3, indicating slightly alkaline to alkaline nature of groundwater. According to the WHO, the range of desirable pH values of water prescribed for drinking purposes is 6.5 – 9.2 (WHO, 2004). There are no water samples with pH values outside of the desirable ranges .

Figure (18) show that difference in Acidity between two springs .

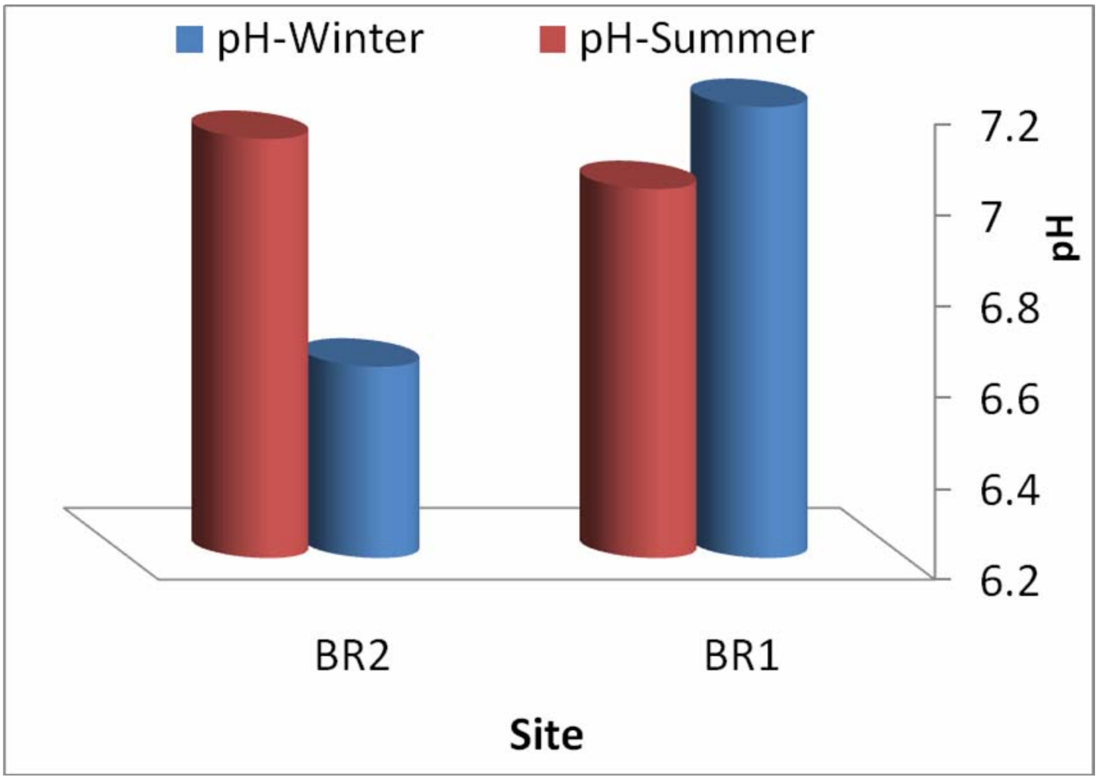


Figure 18

pH acidity in water from Burbeita site at winter and summer season.

Electrical Conductivity

Surface water has a much lower Electrical Conductivity than groundwater because the groundwater has been able to react with the minerals in the soil and rocks in the ground .

As shown in Table (3) the electrical conductivity of the springs at Burbeita ranged from 520 to 720 µS/cm with an average value of 616.8 µS/cm during winter season and from 479 to 570 µS/cm with an average value of 536.3 µS/cm during summer season .

As shown in figure (19) the electrical conductivity of the spring (BR1) in both the seasons were very close to each other indicating that the water is cold and slightly interacting with mineral in the soil and rock.

In summer the electrical conductivity of the spring (BR2) less than in winter due to the temperature did not change dramatically .

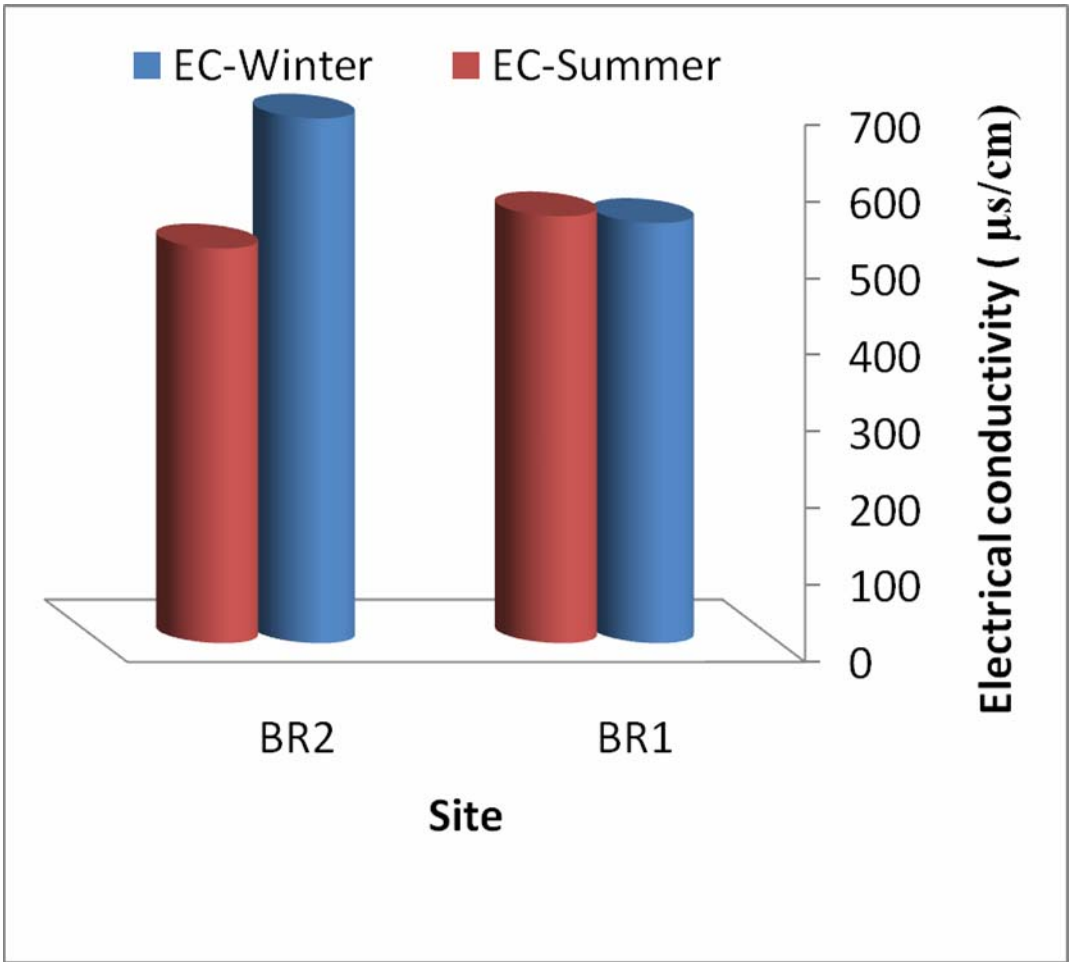


Figure 19
Average Electrical conductivity in water from Burbeita site at winter and summer season.

2.Chemical Parameters
Major Cations
Water Hardness

calcium and total hardness are currently analyzed as an indicators of water quality. The total hardness is defined as the sum of calcium and magnesium ions concentration, both expressed as meq. l^{-1} or mg l^{-1} of calcium carbonate (Saurina et al 2002).

Calcium

As shown in table (3), Ca concentration ranged from 44.78 to 54.8 ppm with an average concentration of 50.07ppm at the end of winter season and from 44.78 to 88.31 with an average concentration of 67.14ppm at the end of summer season.

Figure(20) shows the concentration of Ca ions at two springs location within Burbeita site. It is clear that there was no significant changes in Ca concentrations between summer and winter season for the spring (BR1) but

it was clear at the spring (BR2) which showed a significant increase in Ca concentrations at the end of summer season which reach to 88.31ppm . which can be due to elevated temperature at end of summer that means water from spring (BR2) is able to dissolve mineral from rock and soil which concentrated the calcium.

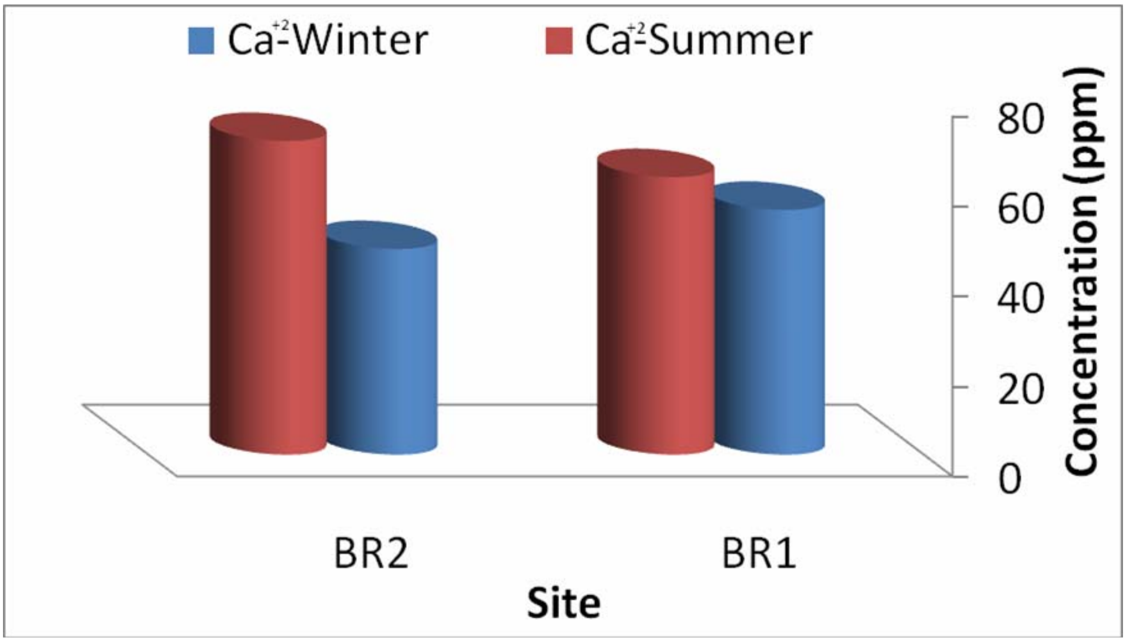


Figure (20)
concentration (ppm) of calcium in two springs water from Burbeita site .

Magnesium

For Magnesium shown in table (3), the concentrations of Mg during winter season ranged from 13.16 to 17.64 ppm with an average concentration of 15.68 ppm. In dry summer season it ranged from 6.21 to 34.29 ppm at spring (BR1) with an average value of 19.29 ppm.

Figure (21) showed the concentrations of Mg for two seasons at two locations from Burbeita site .

It is clear that there was a slight increase of magnesium concentration at spring (BR2) this means that affected according to the season, but increased significantly in cold water at spring (BR1) , this phenomenon gives suggestion that the water reacts with rock long time .

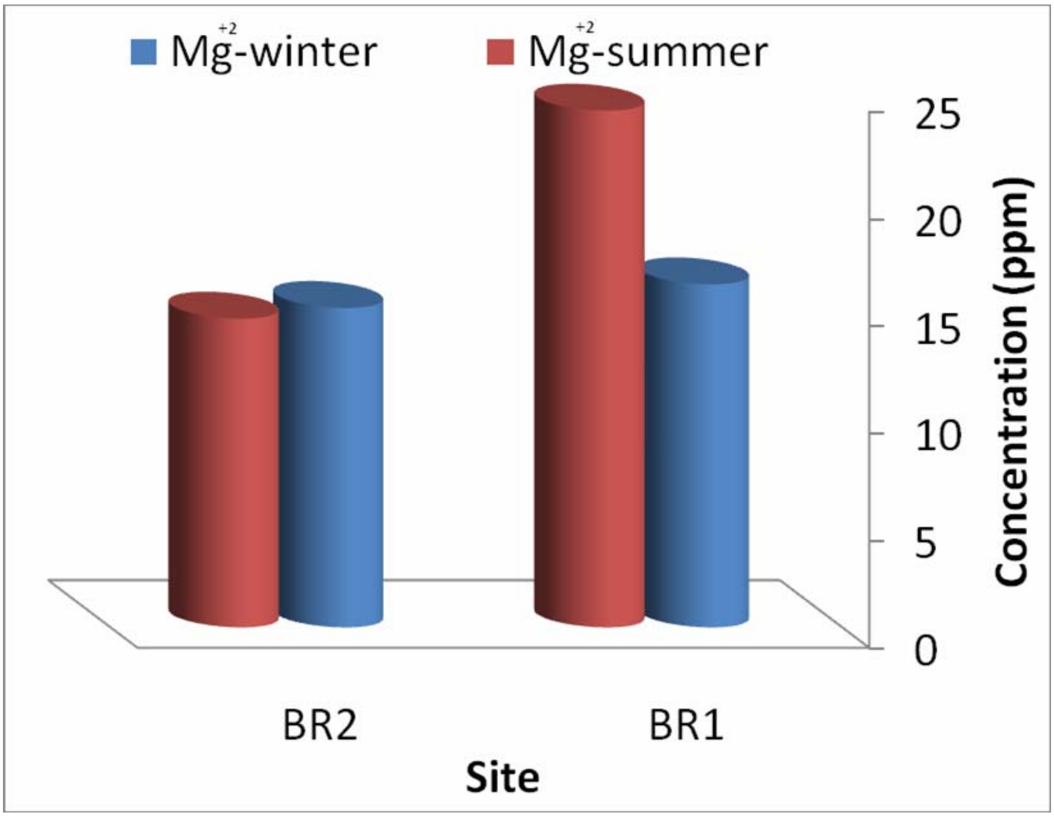


Figure (21)
concentration (ppm) of magnesium in two springs water from Burbeita site .

Sodium

The concentrations of sodium in the thermal springs of Burbeita area was slight differ compared concentration in Afra hot springs water as shown in table (3) it ranged from 33.48 to 35.36 ppm with an average value of 34.06 at the end of winter season and from 33.2 to 42.88 ppm with an average concentration of 38.6 ppm at the end of the summer season.

Figure (21) shows the average concentration of sodium at two sites at Burbeita during both winter and summer seasons.

It is clear that the seasonal variation did not play an important role in the concentration of sodium indicating that the path of water of groundwater flow did not cross sodium rich layers.

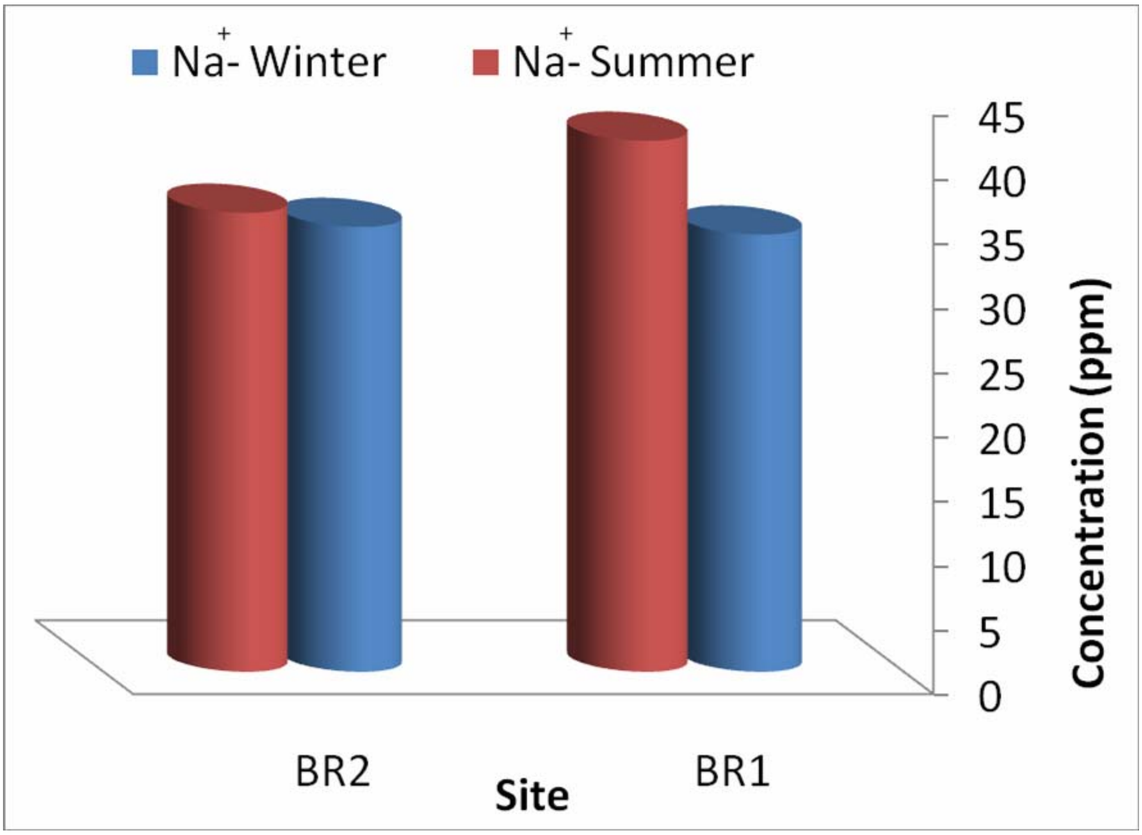


Figure (22)

concentration (ppm) of sodium in two springs water from Burbeita site

Potassium

In all sample were collected from Burbeita area show the concentration of potassium higher than sample from Afra sites.

Tables (3) show The concentration of (K^+) in all sample in Burbeita area where it ranged from 4.3 to 4.78 ppm in (BR2) with an average concentration of 4.435 (rainy season), and 4.32 to 6.84ppm in (BR2) with an average of 5.21 ppm (dry season) .

Figure (23) shows the average concentration of potassium at two sites at Burbeita at the end of both winter and summer seasons. It is clear that the concentrations were very close to each other indicating same main source of potassium .

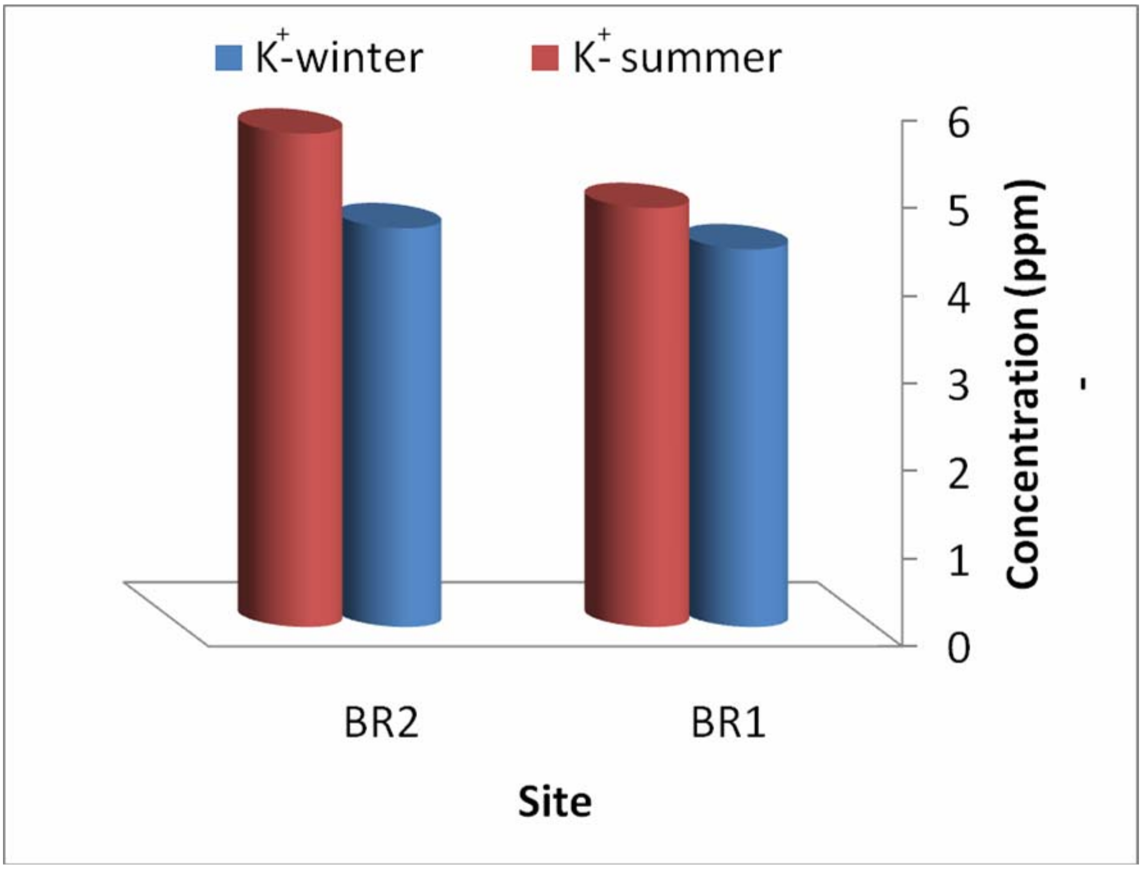


Figure (23)
concentration (ppm) of potassium in two springs water from Burbeita site

3.Major Anions
Bicarbonates

The main source of bicarbonate ions in ground water resulting from the dissolution of limestone and dolomite by water and precipitation (Appelo and Postma,1993) .

The concentrations of HCO_3^- in the thermal springs of Burbeita summarized in Tables (3) as it ranged from 97.11 to 132 ppm with an average value of 112.65ppm at the end of winter season and it ranged from 97.68 to 140 ppm with an average concentration of 118.24 ppm at the end of the summer season.

Figure (24) show the average concentration of HCO_3^- in two sites from Burbita area ,It is clear that the seasonal variation did not play an important role in the concentration of HCO_3^- especially at (BR1), but shows slight variation at (BR2).

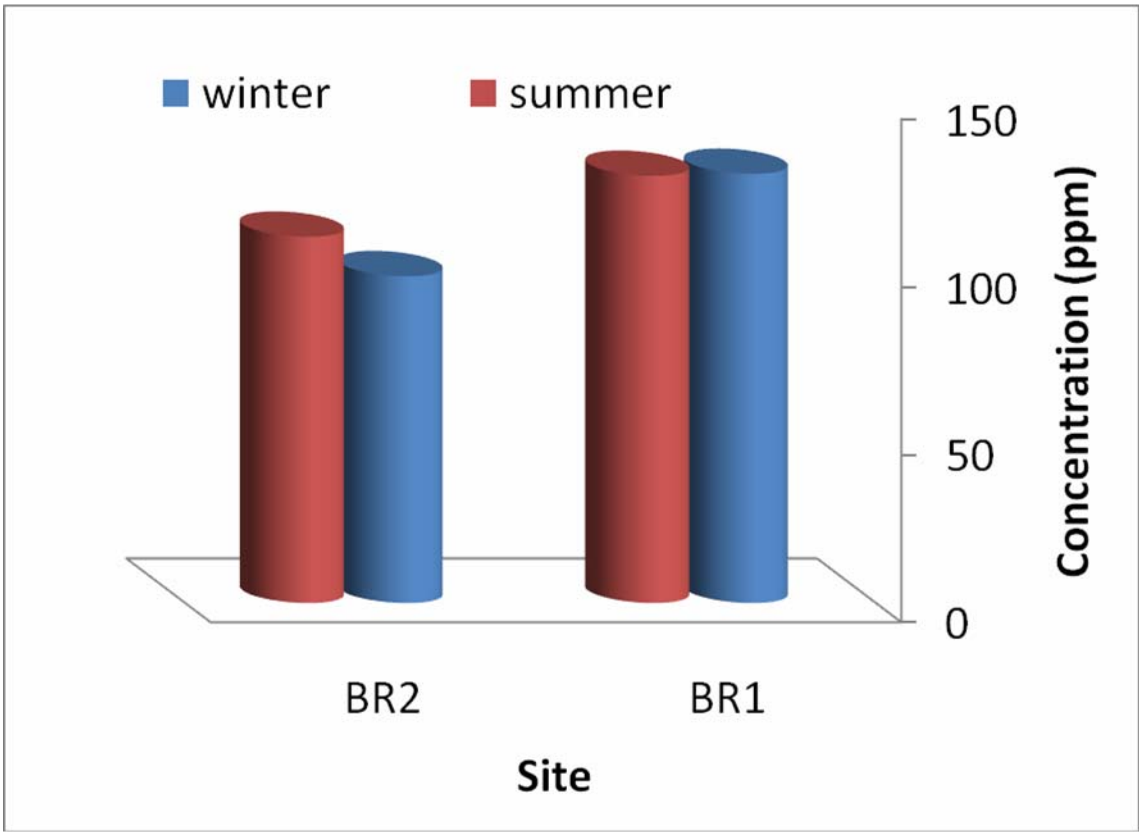


Figure (24)
the average concentration of bicarbonate (HCO_3^-) in two sites at Burbeita area.

Chloride

Chloride is one of the most common ions in water resources as it can be leashed from various rock into soil and water by weathering .

The chloride ion is highly mobile and is transported to closed basins (Appelo and postma,1993) .

The chloride concentration for two springs in Burbeita Table (3) ranged from 66.1 to 200 ppm at sp1 with an average concentrations of 106.83 ppm at the end of the winter season) whereas it ranged from 100 to 132 ppm with an average value of 113.5 ppm at the end of the summer season.

As shown in Figure (25) there was an increase in Chloride concentration during summer season at (BR2), but at (BR1) chloride decrease at end of summer due to the slight variation of temperature .

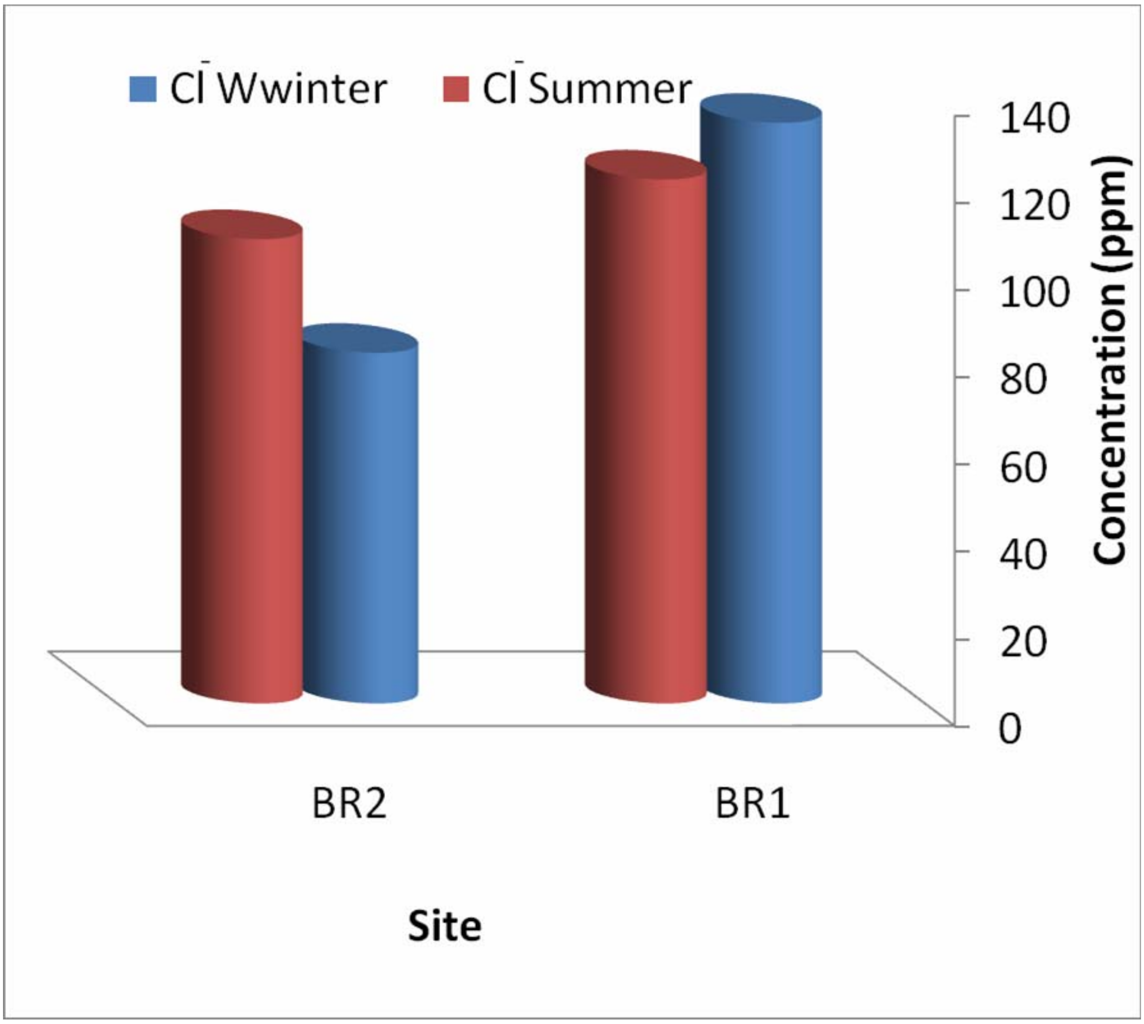


Figure (25)
the average concentration(ppm) of chloride in water from two sites at Burbeita area in summer and winter.

Sulfates

The sulfate concentration is contained in water by originates from chemical weathering of some of the sedimentary rocks such as gypsum. (Appelo and Postma,1993)

As shown in table (3), the sulfate concentrations ranged from an average of 11.76 ppm to 200 ppm with an average concentration of 95.2 ppm at the end of winter season where it decreased at the end of the summer season to concentrations ranging from 30.4 to132 ppm with an average concentration of 67.23 ppm .

As shown in figure (26) The concentration of sulfate in water at (BR1) winter season higher than end of summer , but contrary at (BR2) spring

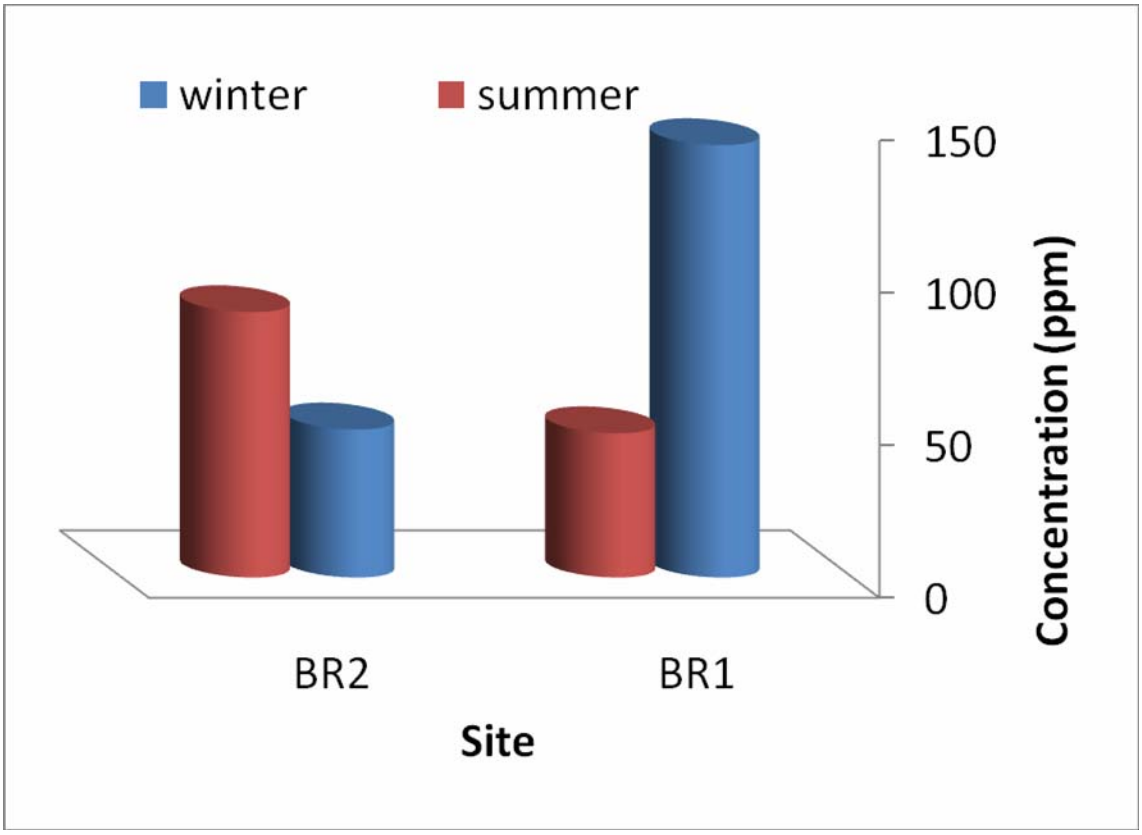


Figure (26)
the average concentration(ppm) of sulfate (SO_4^{-2}) in water from two sites at Burbeita springs .

Nitrate

In all sample were collected from Burbeita sites the concentration of Nitrate slightly variation to samples collected from Afra area .

As shown in Table (3). The nitrate concentrations ranged from 0.1 ppm to 0.53 ppm with an average value of 0.245 ppm at the end of winter season and from 0.18 to 1.13 ppm with an average value of 0.48 ppm at the end of summer season. Figure (27) shows increase concentration in (BR2) at end of summer season and slightly increased in (BR1) at both season .

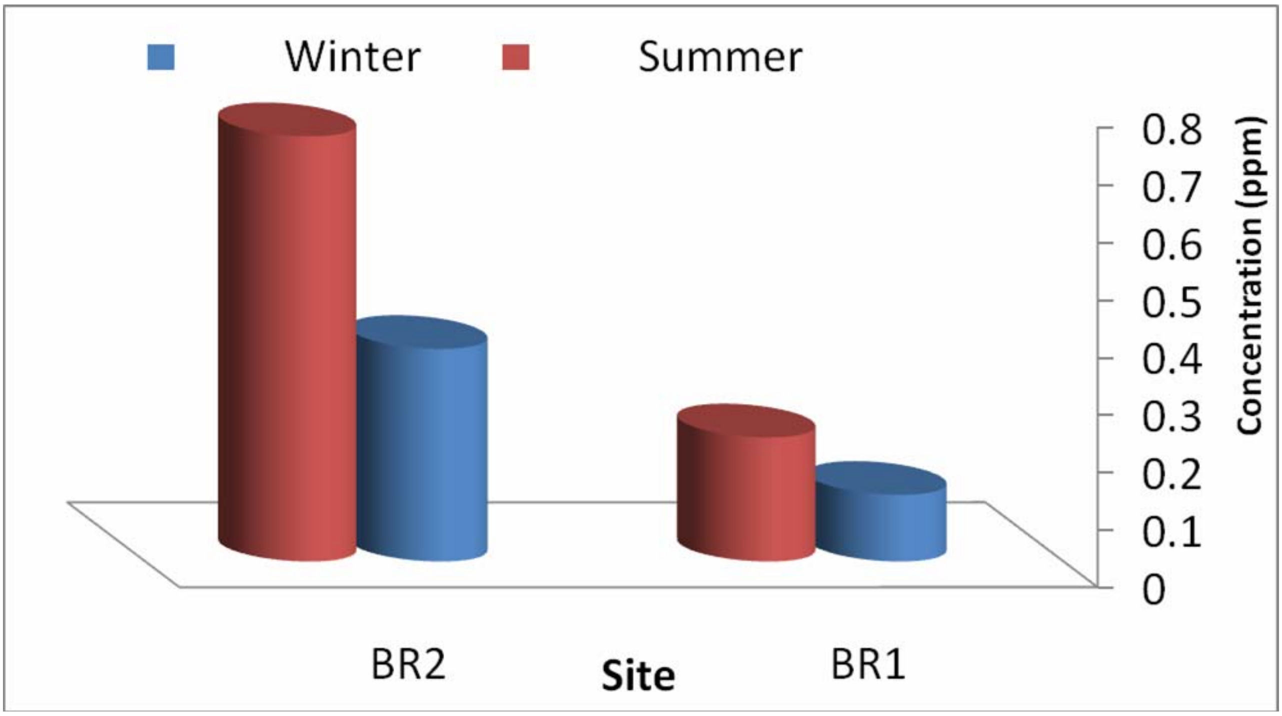


Figure (27)
the average concentration (ppm) of nitrate in water from two sites at Burbeita .

Table 1
Statistical summary of major ionic composition (ppm) and physical parameters of Afra spring at end of winter season.

		Temp	pH	EC	TDS	TH	Na^{+}	Mg^{+2}	K^{+}	Ca^{+2}	SO_4^{-2}	Cl^{-}	HCO_3^{-}	NO_3^{-}
Sp1	Min	40	6.96	550	352	64	31.5	17	2.94	47.1	85	63	90.5	0.04
	Max	42.4	7.29	584	373.7	76.8	35.9	19.1	2.96	57.7	103	90	119	0.07
	Mean	41.3	7.1	564	361	69.9	33.1	18.29	2.95	51.6	92.3	74.3	101.7	0.05
	STD	1.22	0.17	17.7	11.4	6.2	2.43	0.72	0.01	5.47	9.46	14.0	15.2	0.017
Sp2	Min	41	6.9	575	356.4	62.9	34	15.98	2.52	47	44.7	78	99.8	0.13
	Max	44.7	7.04	560	358.4	70.9	34.8	19.1	2.56	51.8	130	100	107.9	0.29
	Mean	42	7	558.3	357.3	66.4	34.4	17.48	2.53	49.3	78.4	86.6	103.2	0.19
	STD	1.85	0.12	1.52	0.97	4.03	0.4	1.56	0.02	2.4	45.4	11.8	4.2	0.087
Sp3	Min	43	7.01	557	356.48	61.7	34.1	14.6	2.52	47.1	62.3	61.3	102.5	0.01
	Max	46.3	7.30	561	359	68.9	36	18.2	2.62	50.7	98.6	102	140.3	0.02
	Mean	44.5	7.15	558.6	357.5	64.9	35	16.4	2.56	48.6	77.6	76.4	116.7	0.013
	STD	1.66	0.15	2.08	1.32	3.66	0.95	1.8	0.06	1.8	18.8	22.3	20.57	0.0057
Sp4	Min	33.3	7.01	488	312	69.8	31.6	16.4	2.5	53.4	88	77	83	0.05
	Max	34.5	7.04	545	348.8	81.1	39.3	20.7	2.59	60.4	110	130	86.3	0.06
	Mean	33.7	7.03	508	325	74.6	34.3	18.8	2.55	55.46	97.6	99	84.43	0.053
	STD	0.64	0.015	32.07	20.52	5.83	4.33	2.18	0.05	4.3	11.3	26.8	1.69	0.006
Sp5	Min	38.3	7.09	494	316	63.7	32.48	14.22	2.29	49.49	50.9	75.6	72	0.04
	Max	38.6	7.37	655	419.2	70.9	32.64	19.11	2.40	51.85	70	100	118.7	0.2
	Mean	38.4	7.21	553	354	66.2	32.54	16.25	2.34	50.64	59.1	85.3	93.56	0.1
	STD	0.15	0.14	88.7	56.78	4.0	0.087	2.54	0.06	1.18	9.8	12.9	23.55	0.087
Sp6	Min	39.8	7.1	503	321.9	48.9	33.4	15	2.5	33.9	60	50.5	127.4	0.04
	Max	41.7	7.21	601	384.6	94.2	35.6	17.6	2.8	76.5	80	64.1	129.5	0.16
	Mean	40.46	7.15	566	362	68.19	34.13	16.2	2.65	51.99	71.6	57.2	128.3	0.093
	STD	1.069	0.055	54.4	34.94	23.39	1.27	1.3	0.19	22.07	10.4	6.8	1.08	0.06
Out let	Min	38.5	7.54	511	327	52.46	33.48	17.681	2.89	34.87	76.4	72	82	0.03
	Max	39.8	7.60	602	385.3	64.77	36.36	19.99	2.90	44.78	100	90	90	0.05
	Mean	39.1	7.57	567.6	363.3	57.1	34.78	18.5	2.8	38.6	86.7	80.6	85.6	0.04
	STD	0.66	0.03	49.4	31.62	6.65	1.46	1.25	0.01	5.39	12.1	9.0	4.06	0.01

Table 2
Statistical summary of major ionic composition (ppm) and physical parameters of Afra spring at the end of summer season

		Temp	pH	EC	TDS	TH	Na^{+}	Mg^{+2}	K^{+}	Ca^{+2}	SO_4^{-2}	Cl^{-}	HCO_3^{-}	NO_3^{-}
Sp1	Mi	44.5	6.95	567	362.9	65.21	32.96	15.72	2.28	49.49	22.8	112	129	0.08
	Ma	46.6	7.44	579	370.56	93.1	33.12	30.0	3.0	63.61	70	130	129.4	0.11
	Mea	45.4	7.16	572.7	366.5	82	33.03	22.6	2.61	55.8	46.4	119	129.2	0.10
	STI	1.08	0.25	6.02	3.86	14.9	0.08	7.15	0.36	7.17	23.6	9.64	0.2	0.02
Sp2	Mi	42.9	7.04	566	362.2	77.54	33.44	25.72	2.64	51.82	64.7	113	90.2	0.37
	Ma	44.3	7.41	574	367.4	80.43	35.16	28.58	3.6	51.85	68	129	91.72	0.46
	Mea	43.5	7.2	570	364.8	78.36	34.12	26.86	3.03	51.82	65.9	119	90.97	0.41
	STI	0.72	0.19	4	2.56	1.80	0.91	1.5	0.5	0.01	1.82	8.7	0.76	0.05
Sp3	Mi	46.8	6.8	566	362.2	59.5	33.2	5.72	2.68	44.78	66.7	107	95.9	0.02
	Ma	47.2	7.38	569	364.16	77.05	34.8	22.86	2.8	54.19	72.4	119	102.7	0.04
	Mea	46.9	7.09	567.3	363	65.05	33.83	14.38	2.73	48.42	69.7	112	98.23	0.03
	STI	0.23	0.29	1.57	0.99	13.46	0.85	8.57	0.06	5.05	2.86	47.7	42.56	1.58
Sp4	Mi	35.7	7.08	493	315.5	58.56	31.08	11.43	2.64	47.13	56.5	119	78	0.09
	Ma	36.5	7.55	495	316.8	67.54	31.64	20.0	2.68	56.54	64.2	124	79.8	0.11
	Mea	36	7.39	494	316.2	65.4	31.31	16.69	2.66	52.02	59.3	121	78.66	0.1
	STI	0.43	0.27	1	0.65	6.06	0.29	4.32	0.02	4.72	4.26	2.65	099	0.01
Sp5	Mi	41	6.99	564	360.9	71.85	31.8	20	2.44	51.85	52.4	125	88.3	0.32
	Ma	42.6	7.3	570	364.8	82.26	32.72	25.72	2.48	56.52	85	135	92.4	0.41
	Mea	41.8	7.16	566.3	362.4	75.84	32.27	22.27	2.46	53.60	64.7	129	89.9	0.36
	STI	0.8	0.16	3.2	2.07	5.59	0.46	3.03	0.02	2.55	17.7	5.29	2.19	0.05
Sp6	Mi	39.6	7.32	564	360.96	61.35	33	7.15	2.52	54.2	25.8	112	101.1	0.06
	Ma	42	7.85	570	364.8	111.9	35.24	27.15	2.84	84.82	109	140	120.5	0.17
	Mea	40.9	7.55	567.3	363	90.46	34.08	19.96	2.65	70.50	65.1	123	108.4	0.1
	STI	1.21	0.27	3.05	1.95	26.13	1.12	11.12	0.17	15.4	41.9	14.9	10.55	0.06
Out let	Mi	42.3	7.54	536	360.3	70.4	34.68	9.13	2.76	61.26	51.2	114	106	0.07
	Ma	44	7.71	570	364.8	88.25	35.56	22.85	2.92	65.4	106	137	118.7	0.13
	Mea	43.1	7.58	567	362.9	81.3	35.14	17.49	2.82	63.82	74.6	122	110.7	0.1
	STI	0.85	0.11	3.6	2.3	9.45	0.44	5.99	0.09	1.83	28.3	13	6.96	0.03

Table 3

Statistical summary of major ionic composition (ppm) and physical parameters of Burbeita spring at the end of summer and winter seasons

		Temp	pH	EC	TDS	TH	Na^{+}	Mg^{+2}	K^{+}	Ca^{+2}	SO_4^{-2}	Cl^{-}	HCO_3^{-}	NO_3^{-}
	Min	28.2	6.68	546	349.44	86.83	40.36	11.43	4.32	56.56	30.4	110	115.45	0.18
BR1	Max	31	7.33	570	364.8	90.85	42.88	34.29	5.48	61.7	66.4	132	140	0.26
	Mean	29.9	7.01	557.3	356.69	88.69	41.36	24.14	4.78	47.79	47.36	120.3	127.3	0.216
	STD	1.41	0.325	12.05	7.71	2.02	1.28	11.64	0.616	9.7	18.08	11.06	12.29	0.040
	Min	42	6.57	479	306.56	74.78	33.2	6.21	4.9	44.78	49.29	100	97.68	0.49
BR2	Max	44.3	7.4	546	349.44	95.46	37.48	30	6.84	88.31	132	110	131.6	1.13
	Mean	43.1	7.15	515.3	329.81	84.18	35.74	14.45	5.2	69.72	87.09	106.6	109.16	0.74
	STD	1.15	047	33.85	21.66	10.46	2.25	13.47	1.05	22.45	41.8	5.77	19.43	0.34
	Min	27.7	7.12	520	332.8	69.36	34.2	15.16	4.30	54.2	82.67	66.4	124.5	0.1
BR1	Max	28.7	7.25	592	378.9	71.24	35.6	17.64	4.33	54.8	200	200	132	0.14
	Mean	28.2	7.19	548.6	351.16	70.36	34.68	16.42	4.31	54.43	141.9	133.3	127.9	0.116
	STD	0.577	0.065	38.17	24.59	0.94	0.73	1.24	0.015	0.32	58.67	66.8	3.77	0.02
	Min	41.4	6.5	646	413.4	57.94	33.48	13.16	4.34	44.78	11.76	66.1	97.11	0.26
BR2	Max	42.8	6.76	720	460.8	63.3	35.1	16.17	4.78	47.13	80	100	97.68	0.53
	Mean	41.9	6.62	685	438.36	60.646	34.55	14.93	4.55	45.71	48.6	80.5	97.4	0.37
	STD	0.757	0.13	37.16	23.8	2.68	0.92	1.57	0.22	1.247	34.44	17.5	0.28	0.140

Heavy Metals

Water

As shown in table 4 and figure (28) that the heavy metals concentrations were relatively low which can be attributed to neutral pH enhancing precipitation of metals from the aqueous phase to the solid phase (Jiries et al. 2003). The average concentrations of heavy metals for Afra site for summer season were 132.4, 54.6, 40.9 and 427.6 ppb for Co, Ni, Cu, and

Fe and the average concentrations were 32.7, 25.4, 47.7, 49.7, and 539.8 for Co, Zn, Ni, Cu, and Fe for winter season respectively.

The average heavy metals concentration at Burbeita site (table 5) were 26.7, 44.8, 46.3and 436.3 ppb for Co, Ni, Cu, and Fe in summer , and 71.7, 18.8, 46.3, 52.8, and 506.1 for Co, Zn, Ni, Cu, and Fe for winter season respectively.

As shown in figures (28) and (29) that the abundance of metals at both sites showed similar and they were in descending order Fe> Co > Ni>Cu >Zn while Cr was not detected in any sample.

Table 4
Statistical summary of heavy metals concentrations (ppb) for Afra Site (n=4).

Site		Summer						Winter					
		Co	Zn	Ni	Cu	Cr	Fe	Co	Zn	Ni	Cu	Cr	Fe
SP1	Min	26	ND	43	24	ND	180	33	10	30	42	11	430
	Max	108	ND	74	46	ND	420	106	25	74	63	13	450
	Mean	67	ND	58.5	35	ND	320	66.3	17.5	45.3	50	12	440
SP2	Min	45	ND	33	22	ND	240	11	12.5	29	29	ND	560
	Max	69	ND	52	46	ND	610	33	24	52	58	ND	620
	Mean	57	ND	42.5	34	ND	390	22	18.3	39	45.7	ND	593
SP3	Min	24	ND	45	21	ND	232	17	1.3	29	36	ND	580
	Max	241	ND	80	53	ND	688	30	31	70	57	ND	670
	Mean	128.3	ND	62.5	37	ND	462	22.3	16.2	49.3	44.7	ND	630
SP4	Min	58	ND	32	13.2	ND	269	14	13.5	29	34	ND	460
	Max	110	ND	62	59	ND	784	31	36	61	57	ND	700
	Mean	84	ND	47	36.1	ND	534.3	22.5	24.8	50	48.3	ND	590
SP5	Min	110	ND	54	34	ND	320	25	59.8	6	45	ND	470
	Max	210	ND	81	66	ND	476	42	60	80	66	ND	510
	Mean	160	ND	67.5	50	ND	402	33.5	59.9	53.3	58.3	ND	493
SP6	Min	112	ND	32	53	ND	250	18	10	24	41	ND	380
	Max	470	ND	67	53	ND	700	35	21	80	68	ND	630
	Mean	304	ND	49.5	53	ND	420.3	26.5	15.5	57	52	ND	510
Out let	Min	130	ND	54	40	ND	142	38	32	32	50	ND	300
	Max	245	ND	82	70	ND	648	110	86	65	57	ND	650
	Mean	181	ND	65.3	48.3	ND	349.6	74.3	54	44	53	ND	466

***ND : Not detect .**

Table 5
Heavy metals concentration in (ppb) for water samples collected from Burbeita site (n=4).

		Summer						Winter					
		Co	**Zn**	**Ni**	**Cu**	**Cr**	**Fe**	**Co**	**Zn**	**Ni**	**Cu**	**Cr**	**Fe**
BR1	Min	10.0	ND	45.0	33.0	ND	364.0	37.0	0.8	32.0	45.0	ND	200.0
	Max	30.0	ND	73.0	68.0	ND	780.0	84.0	31.0	42.0	46.0	ND	290.0
	Mean	20.0	ND	59.0	50.5	ND	531.3	62.0	11.5	36.7	45.7	ND	246.7
	Min	10.0	ND	2.0	23.0	ND	212.0	42.0	0.5	38.0	52.0	ND	400.0
	Max	60.0	ND	59.0	61.0	ND	410.0	131	42.0	76.0	69.0	ND	1150.0
BR2	Mean	30.0	ND	30.5	42.0	ND	320.7	74.3	26.8	53.0	59.0	ND	750.0

*ND : Not detect .

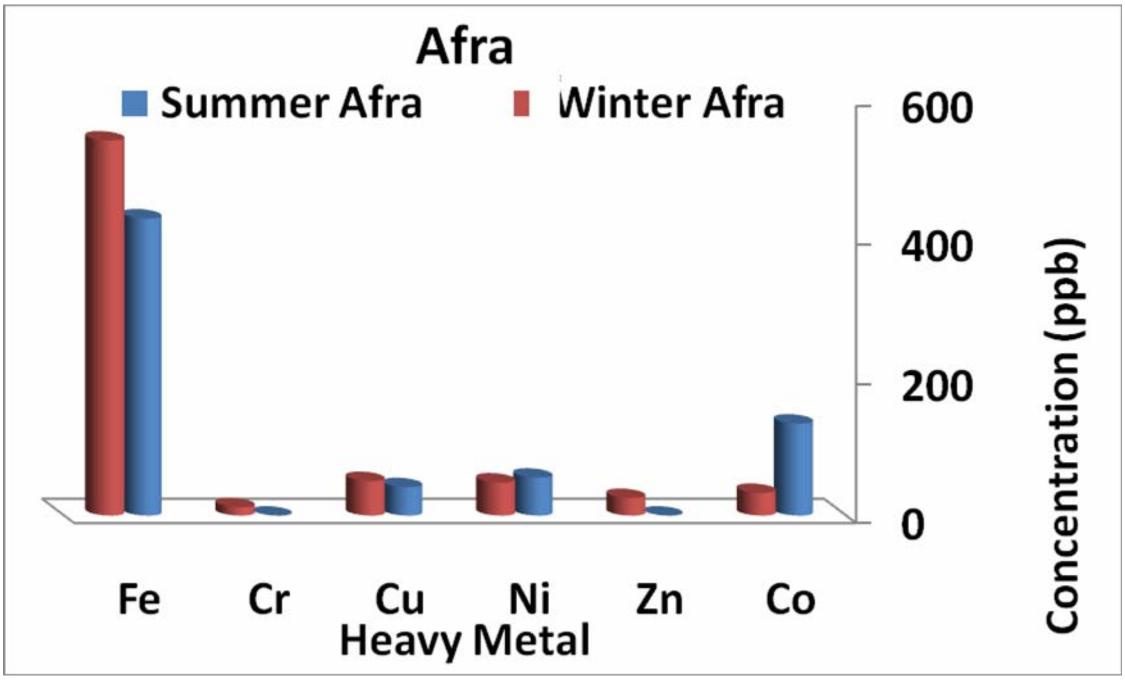


Figure (28)
Heavy metal concentration (ppb) for water samples collected from Afra site at winter and summer season.

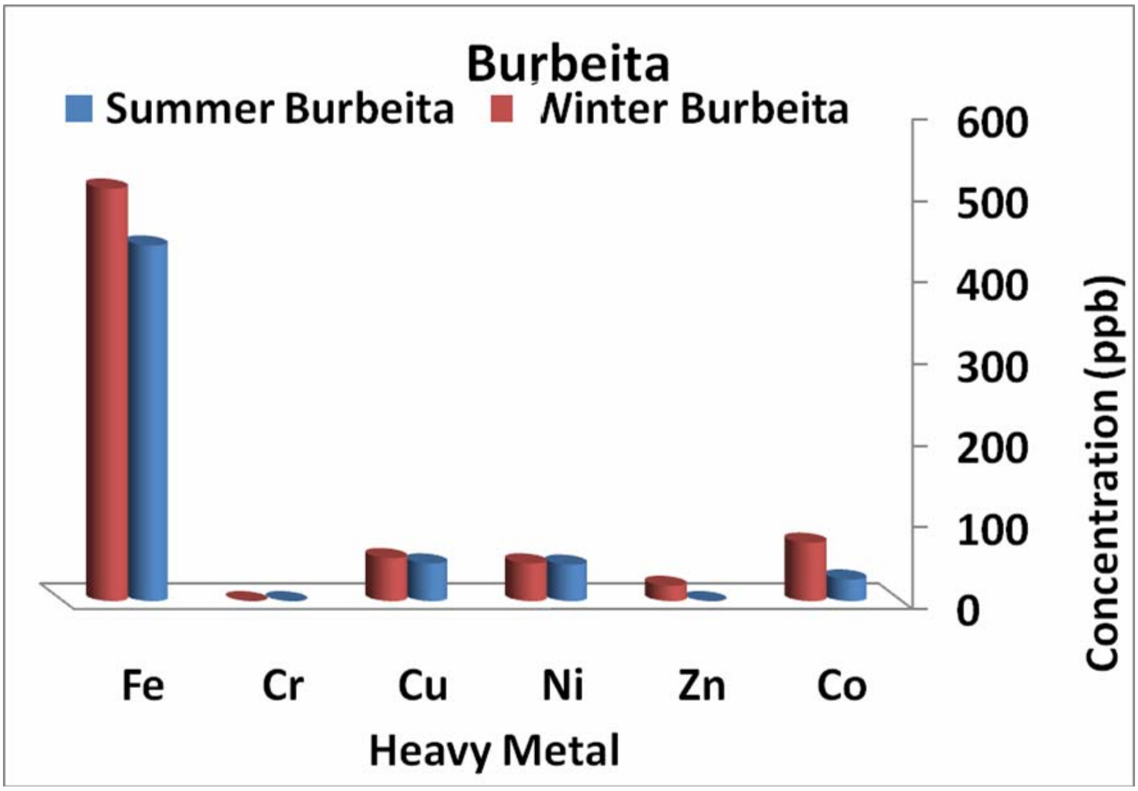


Figure (29)
Heavy metal concentration (ppb) for water samples collected from Burbeita site at winter and summer season.

4.6.Soil

The results of heavy metals concentrations in soil irrigated with the effluent water from both sites are presented in (table 6) . The results showed that the concentration of heavy metals in soil were relatively low which can be attributed to its low concentration in water. There was an inverse relationship between heavy metals concentration in soil with water as some heavy metals which were found below detection limit in the aqueous phase were the highest in the soil indicating its precipitation to the soil surface. The concentration of heavy metals were variable with soil depth which is due to the texture and compaction of the soil which was not homogeneous in the area.

Table 6
Heavy metal concentration(ppb) for soil irrigated by Afra and Burbeita hot spring water and Blank soil

Site	depth	Afra					Burbeita				
		Co	Cr	Zn	Cu	Ni	Co	Cr	Zn	Cu	Ni
1	0-10	198	777	450	215	211	241	759	358	131	193
	10-20	186	647	277.7	182	220	177	335	108	107	108
2	0-10	181	530	334	175	160	138	149	267	119	76
	10-20	191	652	286	162	176	146	81	347	252	110
3	0-10	211	627	231	146	190	148	220	160	146	93
	10-20	263	652	385	179	223	136	207	140	142	120
4	0-10	254	552	420	246	202	163	322	285	215	109
	10-20	227	497	137	147	198	210	544	336	198	123
5	0-10	200	200	198	158	171	173	569	440	206	140
	10-20	206	168	199	147	135	212	454	278	193	154
Blank	0-10	167	160	190	89	119					
Soil	10-20	110	170	178	90	130					

4.7.Wilcox diagram

Wilcox diagram for classification of groundwater was used to evaluated suitability of the spring water at both sites Afra and Burbeita for irrigational purposes Figure (30). The results showed that all collected water samples were classified as(C2-S1) classes. However, the water was of medium conductivity and low sodium adsorption ratio(SAR) . the result show that SAR <1.77 in all collected sample in both site, and the quality of water is Excellent (Richard 1954) . so Due to low sodium and medium salinity water of C2-S1 class can be used in irrigation of almost all soils with no danger of sodium problem.

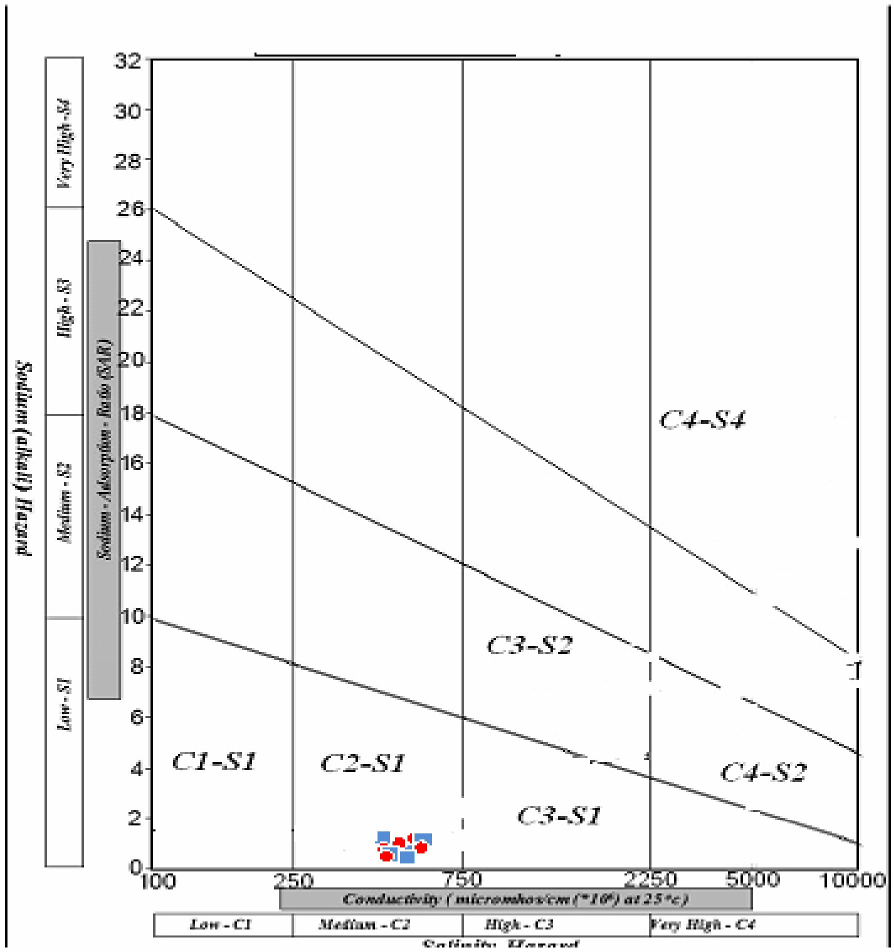


Figure 30:
Wilcox diagram for classification of spring water collected from Afra (■) and Burbeita (●) site. (After Wilcox 1955).

4.8. Piper Diagram

Hydrochemical faces are distinct zones that have cation and anion concentrations describable within defined composition categories. Piper diagram is one of the most useful ways of representing and comparing water quality. In the Piper Diagram cations, expressed as percentages of total cations in mill equivalents per liter plots as a single point on the left triangle and anions

Geochemical graphic analyses methods for all water samples by using Piper diagrams has been widely used in groundwater studies to characterize large number of water chemical data. Major ions data was plotted on the Piper diagram as shown in (Fig 31). The Piper classification of drinking water in both thermal springs sites shows that most of the water samples can be considered as calcium magnesium type with prevailing sulfate and chloride.

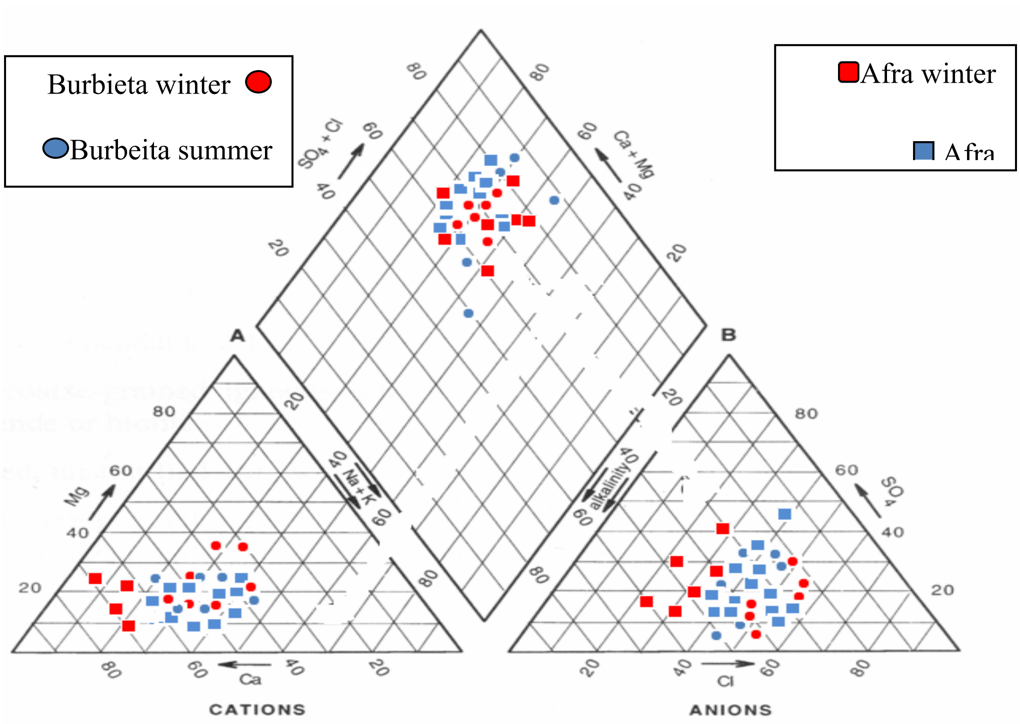


Figure (31):
Piper diagram for Afra and Burbeita springs wate

4.9 Conclusions and Recommendations

Based on the results of this study the following can be concluded

1. The temperature of the thermal springs at both Afra and Burbeita did not show variation with seasons.
2. The pH values of water collected from different locations at Afra sites were near to neutral condition due to buffering effect action of dissolved minerals especially carbonate rocks
3. The electrical conductivity of the thermal water in both the seasons were very close to each other indicating that the rainy season do not play an important role in the water salinity
4. The outlet at Afra site showed a significant increase in Ca^{+2} concentrations at the end of summer season which can be due to evaporation of the thermal water during hot and dry summer conditions increased with the high temperature of the thermal water.
5. Nitrate ion concentrations were low indicating that there was no source of pollution in the investigated area.
6. The water type of both sites can be considered as calcium magnesium type with prevailing sulfate and chloride.
7. The water quality was of medium electrical conductivity and low sodium hazard indicating that the water can be used for irrigational purposes without risk.

8. Heavy metals concentrations were low in all water samples which was due to neutralized pH values.
9. The abundance of metals at both sites showed similar and they were in descending order Fe> Co > Ni>Cu >Zn and Cr was not detected in any sample.
10. There was an inverse relationship between heavy metals concentration in soil with water . As some heavy metals found below detection limit in the aqueous phase were the highest in the soil indicating its precipitation to the soil surface.
11. The concentration of heavy metals was variable with soil depth which is due to the texture and compaction of the soil which was not homogeneous in the area.

It is recommended that the water can be used for drinking purposes too if no other pollutants exist .

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